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MERCURY RECOVERY FROM CONTAMINATED WASTE WATER AND SLUDGES

Richard Perry

Georgia-Pacific Corporation

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MERCURY RECOVERY FROM CONTAMINATED WASTE WATER AND SLUDGES

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Richard Perry

12040 HDU

Georgia-Pacific Corporation, Bellingham Division

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xxxxxxxxxxxxx Abstract: A plant was designed, built and operated to remove Hg from waste water and sludge produced by a mercury cell chlor-alkali plant. Mercury content of the waste water ranged from 300 - 18,000 ppb mercury while mercury content of the brine sludge ranged from 150 to 1500 ppm Hg. Other sludges processed include sludges from the waterway near our plant outfall with a Hg content of 10 - 25 ppm Hg.

From a variety of removal techniques tried in the lab, the methods selected were sulfide precipitation for the water treatment and high temperature roasting for the sludge treatment. The sulfide precipitation consists of collecting the various water streams, adjusting the pH from 5 - 8 with spent sulfuric acid, settling the large solid particles in a surge tank, adding sodium sulfide to a 1-3 ppm excess, adding diatomaceous earth at the rate of 0.07 gpl in an R. P. Adams pressure filter. The effluent Hg levels range from 10-125 ppb with an average of 50 ppb Hg for an 87-99% removal, averaging 96.8%. The 4.8m^3 filter handles 280-280 liters/min adequately with an approximate 48 hour cycle time between backwashings. Capital costs were $143,900 and operating costs were 50¢/378$ l

The sludge system contains a collection system, 3.7 m diameter thickener, 1.8 m diameter rotary vacuum filter, 1.37 m i.d. multiple hearth furnace, and 3 stainless steel condensers 21 m^2 each. Processing rate for the sludge is 140-320 kg/hr, dry basis. At present we are processing approximately 18 m tons of sludge per month for our Chlor-Alkali Plant. Operating temperatures ranged from 540 C - 760 C, feed Hg content ranged from 290 to 440 ppm Hg (dry basis), and clinker Hg content after treatment contained 0.5 - 7.2 ppm Hg, for a removal rate of 98.3 to 99.8%. Waterway sediments containing 12.8 ppm were roasted at 730 C and clinker contained 0.95 - 1.7 ppm Hg for an 87-92% removal. Capital costs were $364,500 and operating costs were $32 per m ton of dry sludge treated.

Water Pollution, Metals, Sludge Disposal, Waste Water Treatment, Sulfides, Chemical Precipitation, Hydrogen Sulfide, Filtration, Electrolysis, Activated Carbon, Ion Exchange, Reduction (chemical) Particle Size, Oxidation, Chlorination

Mercury, Chlor-alkali Cells, Separation, Recovering, Thickening, Clarification, Roasting, Sodium Hypochlorite, Methyl Mercury, Sodium Borohydride, Vacuum Filtration

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By

Richard Perry

Project 12040 HDU

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ABSTRACT

A system was designed, installed and operated to recover mercury (Hg) from waste water and sludge produced by a mercury cell chlor-alkali plant. Hg content of the waste water ranged from 300 - 18,000 ppb while Hg content of the brine sludge ranged from 150 - 1500 ppm Hg. Deposits from the waterway near the plant outfall were also processed.

From a variety of removal techniques evaluated, sulfide precipitation was selected for process water treatment and high temperature roasting for sludge treatment.

The sulfide precipitation system steps include collecting the process water streams, adjusting the pH to 5-8 with spent sulfuric acid, settling the large particles in a surge tank, adding sodium sulfide to a 1 - 3 ppm excess, adding diatomaceous earth at the rate of 0.7 gpl (0.62 lb/1000 gal), and filtering through an R. P. Adams pressure filter. The effluent Hg levels range from 10 - 125 ppb and average 50 ppb Hg, an 87 - 99% removal, averaging 97%. The 44.8 m^2 (169 ft^2) filter processes up to 380 l/min (100 gpm) with an approximate 48-hour cycle time between backwashings. Capital costs totaled $143,900 and operating costs average 50 /3785 l (1000 gal).

The sludge treatment system includes a collection system, a 3.7 m (12 ft) diameter thickener, a 1.8 m (6 ft) diameter rotary vacuum filter, a 1.37 m (4.5 ft) i.d. multiple hearth furnace, and 3 stainless steel condensers 21 m^2 (224 ft^2) each. Processing rate for the sludge is 140 - 320 kg/hr (300 - 700 lb/hr), dry basis. At present, approximately 18 m tons (20 s tons) of sludge per month are processed. Operating temperatures range from 540°C - 760°C (1000°F - 1400°F), feed Hg content ranges from 290 - 440 ppm Hg (dry basis), and clinker Hg content after treatment varies from 0.5 - 7.2 ppm Hg, for a removal rate of 98.3 - 99.8% Waterway sediments containing 12.8 ppm were roasted at 750°C (1350°F) and the clinker contained 0.95 - 1.7 ppm Hg, for an 87 - 92% removal. Capital costs totaled $364,500 and operating costs are $32/m ton ($35/s ton) of dry sludge treated.

This report was submitted in fulfillment of Project Number 12040 HDU by the Georgia-Pacific Corporation, under the partial sponsorship of the Environmental Protection Agency. Work was completed in April, 1974.

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SECTION I

CONCLUSIONS

1. Sulfide precipitation offers several advantages over other methods of Hg removal from water: (a) fewer process steps, (b) pH range compatible with total plant effluent, (c) concentrated Hg products, (d) inexpensive chemicals used, and (e) minimal environmental stress.

2. In the laboratory, sulfide treatment achieved 99.9% removal of Hg from solutions containing 10 - 100 ppm Hg.

3. In the plant, the sulfide process achieved 87 - 99.2% removal from solutions containing 0.3 - 6 ppm Hg. The average effluent Hg content was 50 ppb.

4. The major problem experienced with the sulfide process was pH control. With concentrated sulfuric acid, a two-stage addition system was needed.

5. Sulfide system capacity is 380 l/min (100 gpm). Capital costs totaled $143,900, and operating costs of the sulfide system are 13¢/1000 l (50¢/1000 gal).

6. High temperature roasting was the only method found to remove more than 87% of the Hg to levels lower than 47 ppm in the clinker. All chemical and electrolytic methods tried resulted in less Hg removed.

7. In the plant scale tests, the roasting achieved 98.7 - 99.8% removal down to levels of 0.5 - 7 ppm Hg from feed concentrations of 255 - 440 ppm Hg (dry basis).

8. Successful operation of the sludge treatment system hinges on removal of wood and other large objects in the sludge and careful attention to the sludge conveying methods selected between steps in the process.

9. The capacity of the sludge roasting system is 7.3 m tons (8.0 s tons) per day, dry basis. Capital costs totaled $364,000. Operating costs are $32/m ton ($35/s ton) sludge.

SECTION II

RECOMMENDATIONS

1. Sludge from other chlor-alkali plants should be roasted to determine the efficiency of this process on various wastes. Also, sludges from other industries and municipal sewage plants which contain Hg should be tested.

2. The Hg recovery from the air leaving the furnace requires further work to solve the dust removal problem.

3. To offset the operating cost of the sludge process, potential uses for the calcium and magnesium oxide in the clinker should be investigated.

4. A further step in the water treatment process would be the design of a polishing filter to remove most of the remaining Hg in the filter effluent.

SECTION III

INTRODUCTION

The industrial hygiene problems associated with Hg vapor, and both inorganic and organic Hg compounds have long been recognized and safeguards have been developed to avoid harmful exposures. The situation changed dramatically with the publication in 1968 of the biological conversion of inorganic Hg to methyl Hg and similar compounds. The toxicity, persistence, and concentration of methyl Hg in food chains caused concern for any discharge of Hg into the environment.

Extensive analyses in North America indicated high Hg levels in fish and sediments associated with certain Hg cell chlor-alkali facilities. All facilities in North America rapidly took steps to reduce total Hg discharges to less than 0.23 kg/day (0.5 lb/day) to the receiving waters at each installation. In most instances, this involved stockpiling of Hg-containing materials such as process sludges (Figure 1).

An objective of these studies was to develop a system to reduce the Hg content of brine process sludge and other Hg-containing solids and liquids to a level sufficiently low that they may be disposed of without significant hazard to the environment. A further objective was the recovery of Hg without significant loss into the atmosphere.

The Bellingham Chlor-Alkali plant, Figure 2, went into production in 1965 with a capacity of 122 m tons (135 s tons) per day of chlorine. Brine sludge averaging 1.4 m tons (1.5 s tons) per day resulted from the precipitation of calcium and magnesium compounds from the incoming solar salt, and erosion of graphite from cell anodes. The sludge had been stockpiled in an impoundment basin pending the development of a Hg recovery system. Hg contaminated water is generated at the rate of 110 - 190 l/min (30 - 50 gpm).

The major sources of the brine sludge are: (1) the brine clarifier, (2) the brine filters, and (3) the salt saturator residue. Other Hg-containing solids include: caustic filter backwash, cell residue, and caustic storage tank residues.

Figure 1. The Bellingham Chlor-Alkali Plant and brine sludge pond

Figure 2. The Bellingham Chlor-Alkali Plant with sludge pond and Hg recovery structure

The major sources of Hg-bearing waste water are: (1) floor washings from the cell room, (2) purge streams from the cell end-box wash water recycle systems, (3) purge streams from the brine system, (4) drainage from the caustic filtration area, and (5) water from tank cleaning.

An extensive literature search was conducted before and during the project; the results are included in the reference section.

This is the final report on the project and the work performed from June 1, 1971 to April 30, 1974.

SECTION IV

PROCESS DESIGN

SLUDGE TREATMENT FOR Hg REMOVAL

Laboratory Methods

The chemical oxidation tests performed in the lab were on the scale of 250 - 1000 ml of brine sludge treated in beakers (Appendix A). The sludge roasting tests were carried out in lab furnaces with volumes of 3 liters and 100 liters. The temperature, heating time, and air purge were controlled as described below. The laboratory phase of the project lasted 9 - 10 months before the single process to be used was selected.

Chemical and Electrolytic Oxidation

An extensive investigation was devoted to developing a chemical means of removing Hg from the brine sludge (Appendix A). The alternatives tried involved addition of sodium hypochlorite, chlorine, or electrolysis of brine to generate small bubbles of chlorine gas. These treatments are reportedly used to treat Hg ores as well as chlor-alkali cell wastes. Removal rates of over 99% are claimed for concentrated ores and residual Hg levels of less than 0.1 ppm for chlor-alkali sludge (5, 6, 9).

In this study, the treatments not only dissolved Hg, but significant quantities of other components of the sludge as well, so that Hg separation was not effective. The maximum Hg removal was less than 88% with a minimum Hg in sludge after treatment of 47 ppm (Appendix A).

Due to problems of (1) dissolving components other than Hg, (2) multi-staging to achieve desired percent recovery, and (3) difficulty of the filtration and wash steps between the stages, the chemical alternatives to sludge treatment were abandoned.

Roasting at High Temperatures

The roasting of Hg-bearing solids has been used since ancient times to separate Hg from other material (1). In preliminary tests in a small lab muffle furnace, crucibles of brine sludge were heated to several temperature levels for various lengths of time to determine the approximate temperature and time parameters (Table 1). The

Table 1. KILN TREATMENT OF BRINE SLUDGE & GRAPHITE
(ppm Hg)

	Time, hr.	Temperature °C 121 / °F 250	427 / 800	538 / 1000	649 / 1200
Brine sludge	Start	140	140	140	140
	1	---	4.6	3.7	0.19
	8	---	4.5	3.1	0.06
	16	48	---	---	----
	24	---	4.2	2.5	0.04
Cell graphite	Start	---	4200	---	4200
	5	---	20	---	----
	16	---	----	---	6.2

tests yielded residues ranging from 0.3 - 1.7 ppm Hg. These initial results were 20 - 100 times lower than the lowest residuals achieved by chemical treatment.

Following the preliminary tests, a series of trials were conducted in a large kiln on samples ranging in size from 100 g to over 30 kg (Figure 3). The air rate through the kiln was carefully controlled to remove the vaporized Hg to keep from saturating the vapor phase with Hg. Residuals as low as 0.02 ppm Hg were achieved (Table 2 and Figure 4). Temperatures in the range of 800°C - 900°C (1450°F - 1750°F) were required to achieve Hg residuals below 0.2 ppm.

Furnace Selection

Following these successful lab runs, kiln manufacturers were contacted to verify the data on a pilot scale. Tests were conducted at Bartlett-Snow, Cleveland, and BSP Division of Envirotech, Brisbane, California.

At Bartlett-Snow, a 15 cm (6 in) diameter rotary calciner was operated at 800°C (1475°F) with a residence time of 30 minutes. The minimum Hg level achieved in the tests was 25 ppm Hg, which was significantly higher than the batch kiln test at the same temperature (Table 3). The tests were shifted to a multiple hearth furnace to gain better control over residence time and eliminate short-circuiting.

Two multiple hearth furnace manufacturers were contacted; the BSP Division of Envirotech was selected to test the dewatered brine sludge. Tests run in April and June 1972 in a 33 cm diameter (13 in) batch kiln yielded clinker Hg contents of 0.32 ppm.

From these data, a pilot run was scheduled in July to test the procedure on a 76 cm (30 in) furnace at a higher solids feed rate. At temperatures of 730°C - 760°C (1350°F - 1400°F), the Hg level in the clinker was 3.2 ppm (Table 4). This was not as low as desired; however, in a second test at 870°C - 955°C (1600°F - 1750°F), residuals of .12 - .14 ppm Hg were obtained (Table 5).

From these data, the furnace hearth loading was found to be a maximum of 39 kg/m^2 (8 lb/ft^2) per hour so that a wet solids feed rate of 224 kg/hr (600 lb/hr) would require a 7 m^2 (75 ft^2) furnace. This corresponds to a standard 1.37 m (4.5 ft) i.d. 6-hearth unit with 7.9 m^2 (84 ft^2) hearth area.

Figure 3. Lab kiln test assembly for roasting sludge

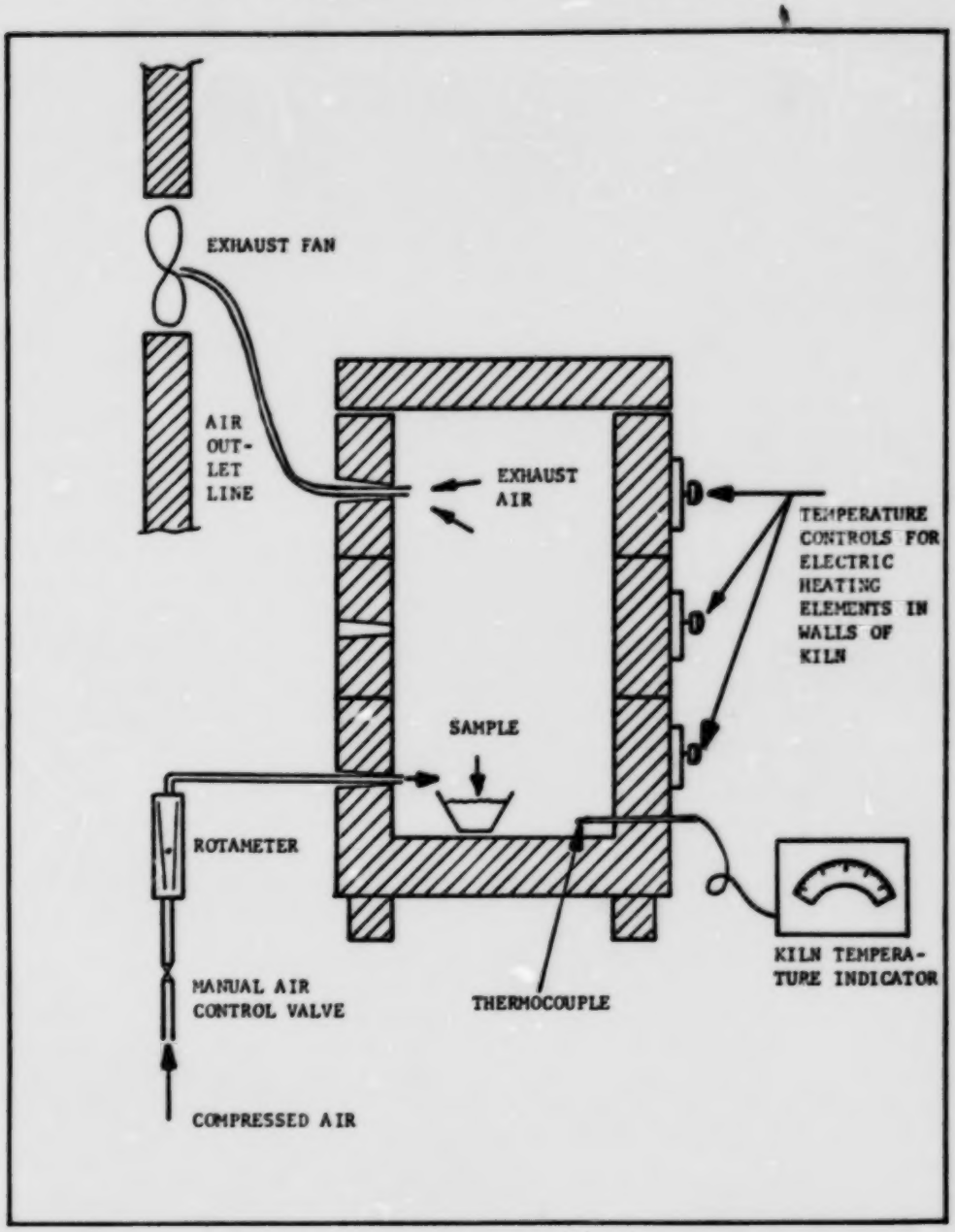


Table 3. KILN ROASTING OF SLUDGE, NO CHEMICAL TREATMENT

Exp. no.	Sample, treatment	Residence time, hr.	Temperature °C	Temperature °F	Agitation, min.	Hg content, ppm Start	Hg content, ppm End	Comments
31	Brine sludge, rotated	8	649	1200	0	---	4.4	
32	"	8	677	1250	0	---	0.4	6 ceramic balls (fine powder)
"	"	8	677	1250	0	---	1.3	" "
33	Brine sludge	8	649	1200	3	---	1.7	
36	"	8	824-38	1525-100	4	500	0.18	NaCl appeared to fuse
42	"	8	774-793	1425-1460	4	---	0.12	
51	"	5	149-260	300-500	9	1340	880	Still slightly wet
"	"	6	232-343	450-650	9	880	50	Still slightly wet
"	"	8	649-760	1200-1400	9	1340	0.5	Top 1" of 9" depth *
"	"	8	649-760	1200-1400	9	1340	4.8	Bottom of 9" depth *
57	"	8	649-760	1200-1400	2	---	0.53	
61	Metal anode sludge	8	649-760	1200-1400	2	158	0.02	
61	Our brine sludge	8	649-760	1200-1400	2	250	0.95	
63	Pond sludge	8	649-760	1200-1400	2	---	0.69	
65	Brine sludge	8	649-760	1200-1400	2	---	0.97	
65	"	8	649-760	1200-1400	2	---	1.7	
70	"	8	649-760	1200-1400	2	246	0.37	pH 10
72	"	8	649-774	1200-1425	2	822	0.47	
72	"	8	649-774	1200-1425	2	1100	0.75	
73	"	8	649-760	1200-1400	2	822	0.07	Excess of air
76	"	8	593-649	1100-1200	2	822	5.21	
79	"	8	593-649	1100-1200	2	822	5.6	
80	"	8	677-718	1250-1325	2	822	2.0	
87	"	5	649-774	1200-1425	2	1735	1.7)	
89	"	8	649-663	1200-1225	2	1735	5.6)	Sludge shipped to Envirotech
90	"	5	538-571	1000-1060	2	1735	14)	7-10-72, 5 barrels for 30"
91	"	7	802-830	1475-1525	2	1735	0.08)	kiln test.
91	"	7	941-969	1725-1775	2	1735	0.03)	
91	Brine sludge from	7	802-830	1475-1525	2	2250	0.07	
91	filter tests	7	941-969	1725-1775	2	2250	0.02	

* Volume decreased to 2/3 upon roasting.

Figure 4. Hg contents of untreated brine sludge after roasting in lab and pilot kilns

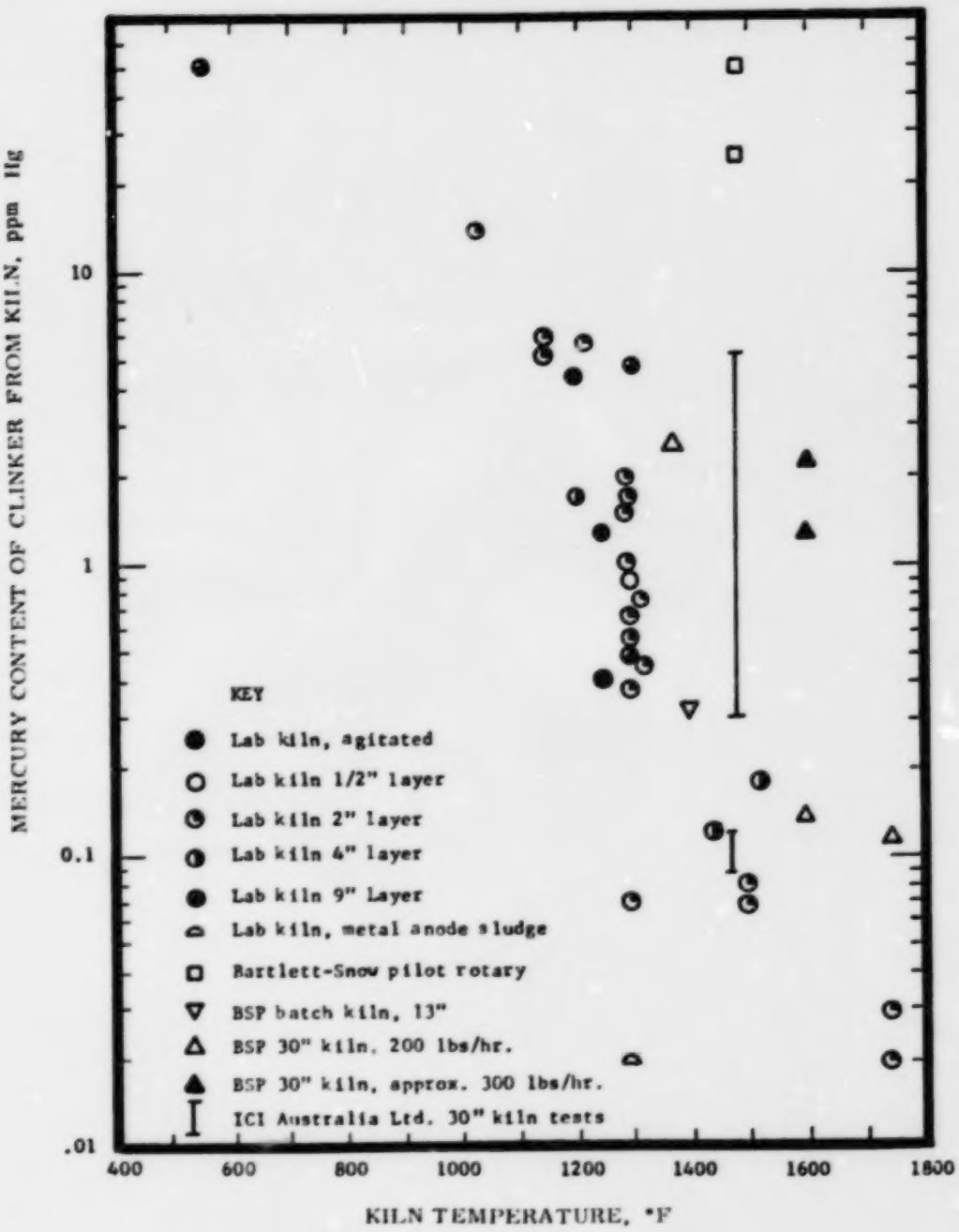


Table 3. ROTARY CALCINER ROASTING OF BRINE SLUDGE

	Run no. 1	Run no. 2 (drying only)	Run no. 3
Hg content of starting material, ppm dry basis	1540	1540	89
Maximum temperature at steady state, °C.	768	357	802
°F.	1415	675	1475
Retention time, min.	30	30	30
Water content of feed, %	30	30	0
Solids feed rate, gm/min.	57	57	57
lb./min.	0.125	0.125	0.125
Purge air rate, standard m^3/hr.	7.4	7.4	7.4
scfh	80	80	80
Screen analysis of solids collected in first 2 hours, % +8 mesh	40	----	59
-8 +60 mesh	31	----	33
-60 mesh	29	----	8
Hg content of screened fractions, ppm +8 mesh	14	----	6.6
-8 +60 mesh	92	----	19
-60 mesh	284	----	93
Hg content of steady state 5 minute sample, ppm	50	89	25
Hg removed, %	96.8	94.2	98.4 Overall
			72 This pass

Table 4. MULTIPLE HEARTH FURNACE ROASTING OF BRINE SLUDGE
BSP 76 cm (30 in) PILOT FURNACE

Test no.	Sample number	Hearth sampled	Hg, ppm	Wet feed rate, kg/hr	Wet feed rate, lb/hr	Retention time, min.
1	1	3	5.7, 5.4	91	200	30
	2	4	11.4, 5.8			
		5	4.8, 4.7			
		6	3.2, 3.4			
2	3	3	5.6	91	200	45
		4	4.7			
		5	4.1			
		6	3.2			
3	4	3	4.1	136	300	30
		4	3.7			
		5	4.3			
		6	4.4			

Test date: 7-24-72
Feed moisture content: 37.6%
Feed Hg content: 1735 ppm, dry basis
Furnace temperature: 760° C. (1400° F.)
Average gas consumption per pound of feed: 0.068 m^3 (2.64 $ft.^3$)

Table 5. MULTIPLE HEARTH FURNACE ROASTING OF BRINE SLUDGE
BSP 76 cm (30 in) PILOT FURNACE

Test no.	Hearth sampled	Hg, ppm	Wet feed rate, kg/hr	Wet feed rate, lb/hr	Temperature, °C.	Temperature, °F.	Retention time, min.
1	3	1.8	91	200	870	1600	30
	4	1.2					
	5	0.31					
	6	0.14					
2	3	1.5	91	200	955	1750	20
	4	0.69					
	5	0.74					
	6	0.12					
3	3	5.6	136	300	870	1600	20
	4	5.1					
	5	2.5					
	6	1.3					
4	3		182	400	870	1600	20
	4	10.7					
	5	4.7					
	6	2.3					

Test date: 8-10-72
Feed moisture content: about 47%
Feed Hg content: 1,735 ppm, dry basis

Since the tests at BSP were run, contacts were made with investigators from an Australian chlor-alkali plant who were also searching for a brine sludge treating method for removing Hg. They also tested the multiple hearth furnace at our suggestion after experiencing unfavorable results from chemical treatment methods. The data from their runs in the 76 cm (30 in) pilot kiln furnace show results similar to ours (Table 6 and Figure 4). Minimum values of 0.1 ppm Hg in clinker were achieved at gas temperatures >800°C (>1470°F).

The multiple hearth furnace is shown in Figure 5. The feed material is conveyed into the top and is carried across the top hearth slowly by the rabble arm plows, then falls to the next hearth. This continues from hearth to hearth until the clinker falls out the bottom of the furnace to be cooled and/or discarded. The heat for the furnace is supplied by gas jets on 2 - 4 hearths and the temperature is controlled by thermocouples and gas flow control valves. Smooth furnace operation with minimum attention is dependent on a constant feed of uniform moisture sludge from the filtering step.

The roasting method should involve the least operator attention of any of the methods considered. The chemical methods studied required many more processing steps with more equipment and more critical control points.

Roasting with Acid Treatment

During the roasting tests a number of variations were tried, including reducing the volume of the sludge so that a smaller kiln could be used to treat the sludge. To reduce the basic sludge, acids were tried successfully. Surprisingly, when acid-treated sludges were roasted, even lower final Hg levels were achieved than for untreated sludge at the same temperature: 0.02 ppm Hg was achieved in the clinker below 760°C (1400°F) (Table 7 and Figure 6). The mechanism is not known although the phenomenon was observed in 31 separate tests.

A patent application has been submitted on this process to the EPA Office of the General Council.

In pilot tests at BSP Division of Envirotech on June 21, 1972, Hg residuals as low as 0.10 ppm were found after 30 minutes at 730°C (1350°F) in their 33 cm (13 in) batch kiln (Table 8).

Table 6. MULTIPLE HEARTH FURNACE ROASTING OF BRINE SLUDGE BSP 76 cm (30 in.) PILOT FURNACE, ICI DATA

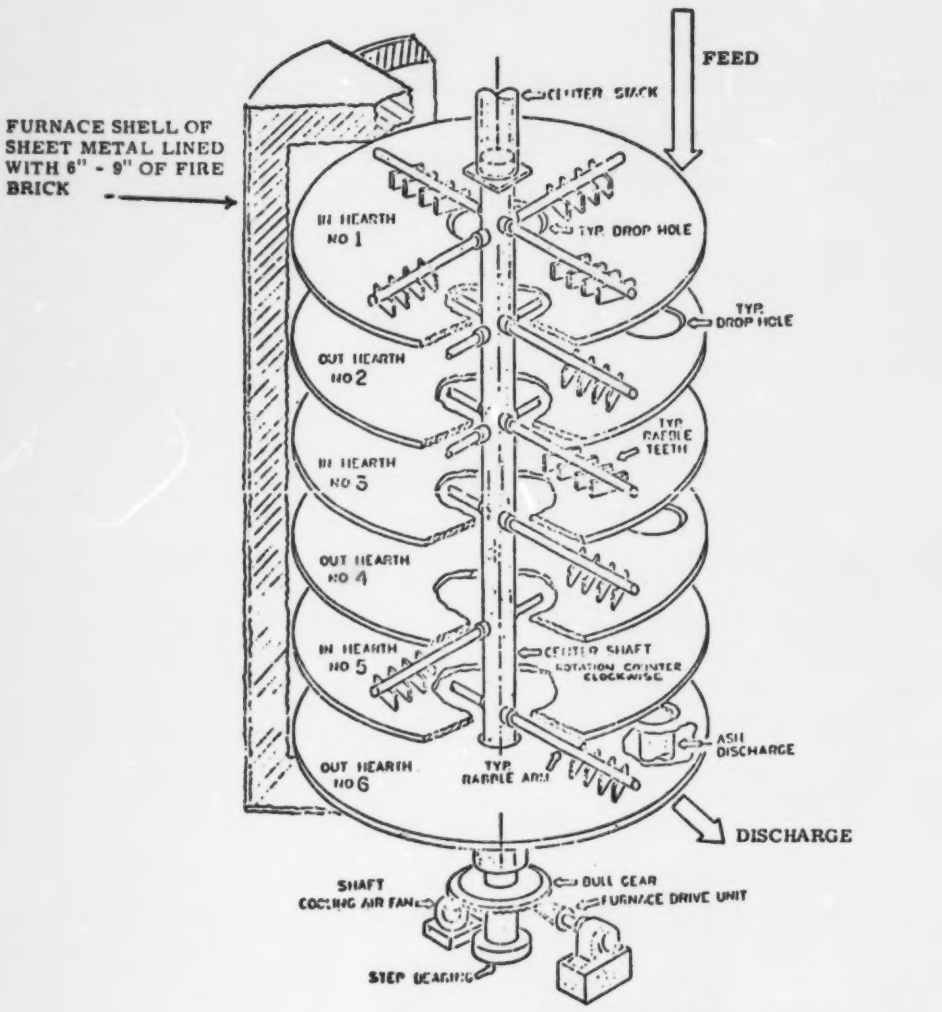
Test no.	Furnace temperature Solids °C.	Solids °F.	Gas °C.	Gas °F.	Hg, ppm Feed	Clinker
1	699	1290	---	----	640	3.8 to 0.5
2a	610	1130	840	1544	640-1200	1.0 to 0.3
2b	538	1000	849	1560	"	8.6 to 0.3
2c	610	1130	840	1544	"	2.2 to 0.6
3	599	1110	921	1690	640	4.0 to 0.1
4	599	1110	799	1470	667	5.7 to 0.3
5	599	1110	799	1470	450	0.1

Test date: 8-29-72
Conditions:

Feed moisture content:	23-38%
Feed rate, dry material discharged:	100-300 lb/hr.
Estimated retention time:	10-30 minutes

Data from ICI Australia Limited Plant Pilot test in Australia.

Figure 5. Cut away drawing of the internals of a multiple hearth furnace showing the rake arms and hearth assembly



FOR THIS DWG. NOTE: RABBLE ARMS ARE NOT SHOWN SLOTED. ONLY FOUR RABBLE TEETH PER RABBLE ARM ARE SHOWN

Table 7. KILN ROASTING OF CHEMICALLY TREATED BRINE SLUDGE

Exp. no.	Treatment	Residence time, hr.	Temperature °C	Temperature °F	Agitation, min.	Hg content, ppm Start	Hg content, ppm End
35	Chlorine pretreated *	8	677	1250	0	113	244.
53	HCl treated	8	649-746	1200-1375	2	230	0.065
61	HCl treated in crucible	8	649-760	1200-1400	2	3660	0.21
63	Cl_2 treated	8	649-760	1200-1400	2	495	0.48
63	HCl treated	8	649-760	1200-1400	2	3660	0.25
65	HCl treated	8	649-760	1200-1400	½	2280	0.26
65	HCl treated	8	649-760	1200-1400	2	2280	0.36
70	Acetic acid to pH 2	8	649-774	1200-1425	2	246	0.26
70	H_2SO_4 to pH 2	8	649-774	1200-1425	2	246	0.05
70	HCl to pH 2	8	649-774	1200-1425	2	246	0.14
70	HCl to pH 2; NaOH to pH 10	8	649-774	1200-1425	2	246	0.37
72	H_2SO_4	8	649-774	1200-1425	2	58	0.02
72	Acetic acid	8	649-774	1200-1425	2	855	0.17
72	HCl	8	649-774	1200-1425	2	563	0.58
72	HCl then NaOH to pH 10	8	649-774	1200-1425	2	764	0.10
73	Acetic acid pH 2-8	8	649-760	1200-1400	2	882	0.08
73	H_2SO_4 pH 2	8	649-760	1200-1400	2	206	0.02
73	HCl pH 2	8	649-760	1200-1400	2	634	0.03
73	HCl pH 0	8	649-760	1200-1400	2	284	0.16
73	HCl pH 3	8	649-760	1200-1400	2	669	0.15
73	HCl pH 0 (60°C.)	8	649-760	1200-1400	2	120	0.06
74	H_2SO_4	8	663-732	1225-1350	2	586	0.06
74	"	8	663-732	1225-1350	2	379	0.02
74	"	8	663-732	1225-1350	2	418	0.01
74	"	8	663-732	1225-1350	2	503	0.05
74	"	8	663-732	1225-1350	2	364	0.10
74	"	8	663-732	1225-1350	2	364	0.002
74	"	8	663-732	1225-1350	2	312	0.22
76	HCl treated	8	593-649	1100-1200	2	585	0.64
76	H_2SO_4 treated **	8	593-649	1100-1200	2	585	4.84
79	H_2SO_4 treated	8	593-649	1100-1200	2	120	0.46
79	" "	8	593-649	1100-1200	2	503	0.10
79	" "	8	593-649	1100-1200	2	364	--
79	" "	8	593-649	1100-1200	2	379	0.13
79	" "	8	593-649	1100-1200	2	418	0.04
80	H_2SO_4 **	8	677-719	1250-1325	2	---	0.09

* Drum rotated 1st hour
** Sent to Envirotech 5/24/72

Figure 6. Acid treatment of brine sludge before roasting in lab and pilot kiln

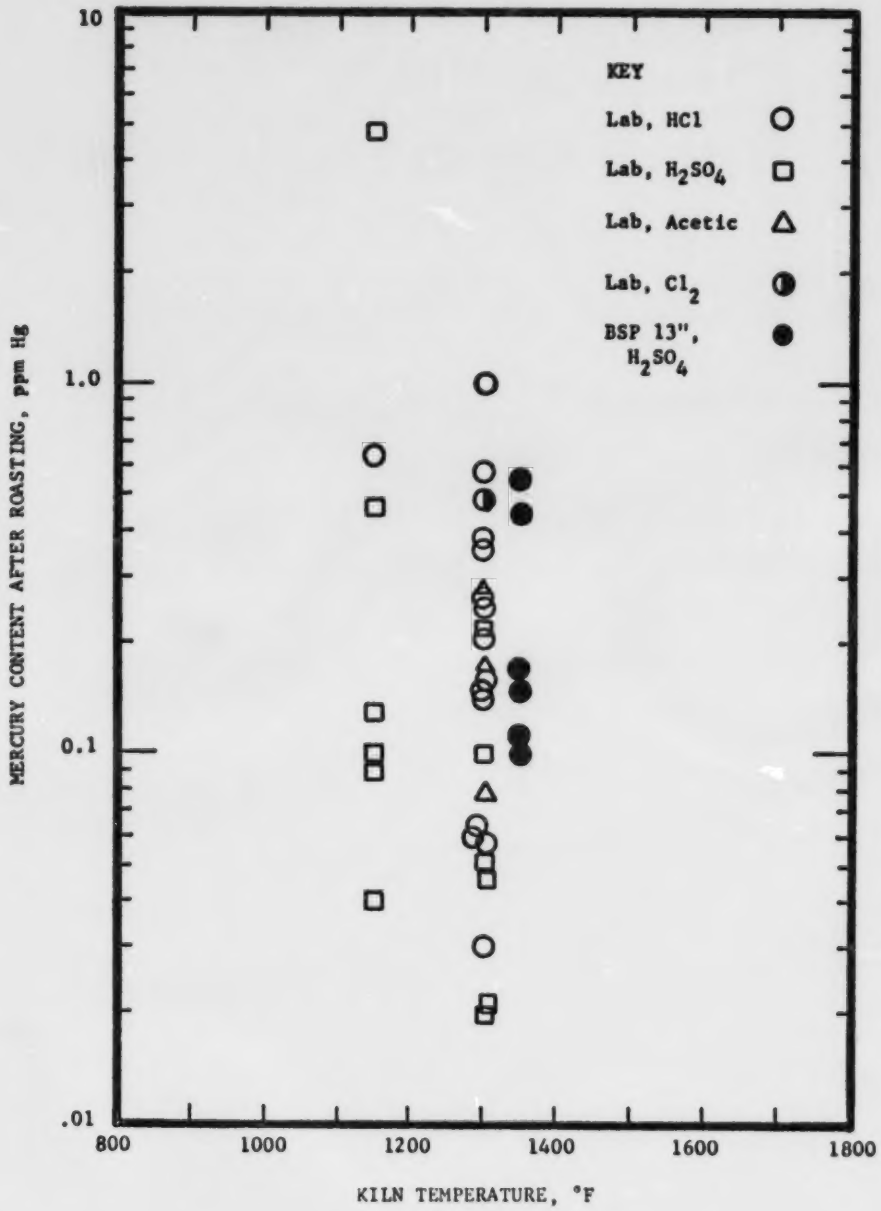


Table 8. BSP TEST ON BATCH KILN

Test no.	Date	Sample treatment	Temperature °C.	Temperature °F.	Retention time, min.	Hg content, ppm Start	Hg content, ppm End
1	4-16-72	Untreated	760	1400	30	874	1.40
		"			60	874	.41
		"			120	874	.42
		"			180	874	.32
2	6-21-72	Acid treated	732	1350	15	620	.55
		"			30	620	.10
		"			45	620	.17
		"			60	620	.45
		"			75	620	.15
		"			90	620	.11

Acid pretreatment was not included in the final process design because heating the untreated sludge an additional 165C° (300F°) achieves the same residual Hg levels at less capital and operating expense. However, the acid pretreatment may be incorporated into the process at a later date if it appears to be necessary due to increased sludge volume or higher than expected residual Hg levels.

Solids Dewatering

The starting material for the sludge processing system is sludge as it comes from the sludge pit. Typically, this sludge is only 5 - 10% total suspended solids as it is pumped from the sludge pit; a 45 - 60% solids feed to the furnace is desirable for economic operation. The dewatering methods tried were: (1) gravity settling, (2) centrifuging, and (3) filtration.

Gravity settling was not satisfactory for this sludge since the maximum concentration achieved was approximately 30% solids.

In lab tests at Barrett Centrifuge, the sludge was dewatered to 72% solids in the first stage and the liquid from the second stage contained 0.2 - 1% insoluble solids (Table 9). However, there may be disadvantages to centrifuging over filtration for this application.

Possible disadvantages are: (1) higher capital cost for equipment for a given capacity, (2) difficulty of obtaining corrosion-resistant material for wetted parts in other than stainless steel, (3) two- to four-stage centrifuging is needed to achieve solids-liquid separation, (4) centrifuges are generally made in only 1 or 2 sizes in each style so that multiple units must be used to achieve required throughputs, and (5) the high speeds of centrifuges with such abrasive and corrosive material as brine sludge could lead to high maintenance. For these reasons, rotary vacuum filtration was selected instead.

The high solids loading indicated that pressure filtration was not feasible. Vacuum filtration was effective on a bench scale. Two standard rotary vacuum filters were tried: a Komline-Sanderson 0.9 m (3 ft) diameter x 1.5 m (5 ft) unit, and an Eimco 0.9 m (3 ft) x 0.3 m (1 ft) unit. As shown in Table 10 and Figure 7, drum rate and solids feed concentration are critical for filter capacity and cake dischargeability. Since filters are available in standard sizes, a filter with an area greater than

Table 9. TEST RESULTS FROM BARRETT CENTRIFUGE ON DEWATERING OF BRINE SLUDGE BY CENTRIFUGING

Sample No.	Test description	Solids by volume, %	Insoluble solids, %	Flow rate thru unit, g pm
1	As received	40	25.6	
	MODEL 912 CENTRIFUGE			
	1 pass	21		1
2	sludge		71.8	
3	supernatant		6.0	
	MODEL 125 CENTRIFUGE (912 Supernatant)			
	1 pass	0.7		1
4	supernatant		1.06	
	3 pass	0.24		1
5	supernatant		0.4	
	5 pass	0.11		1
6	supernatant		0.2	
7	sludge		21.4	

TEST METHOD

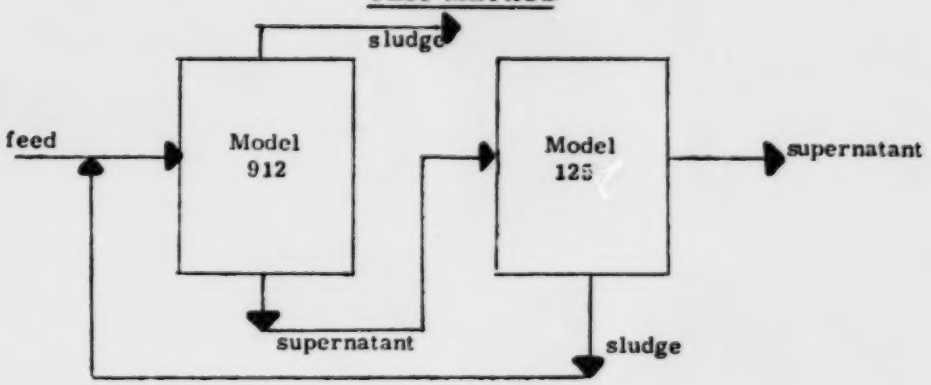
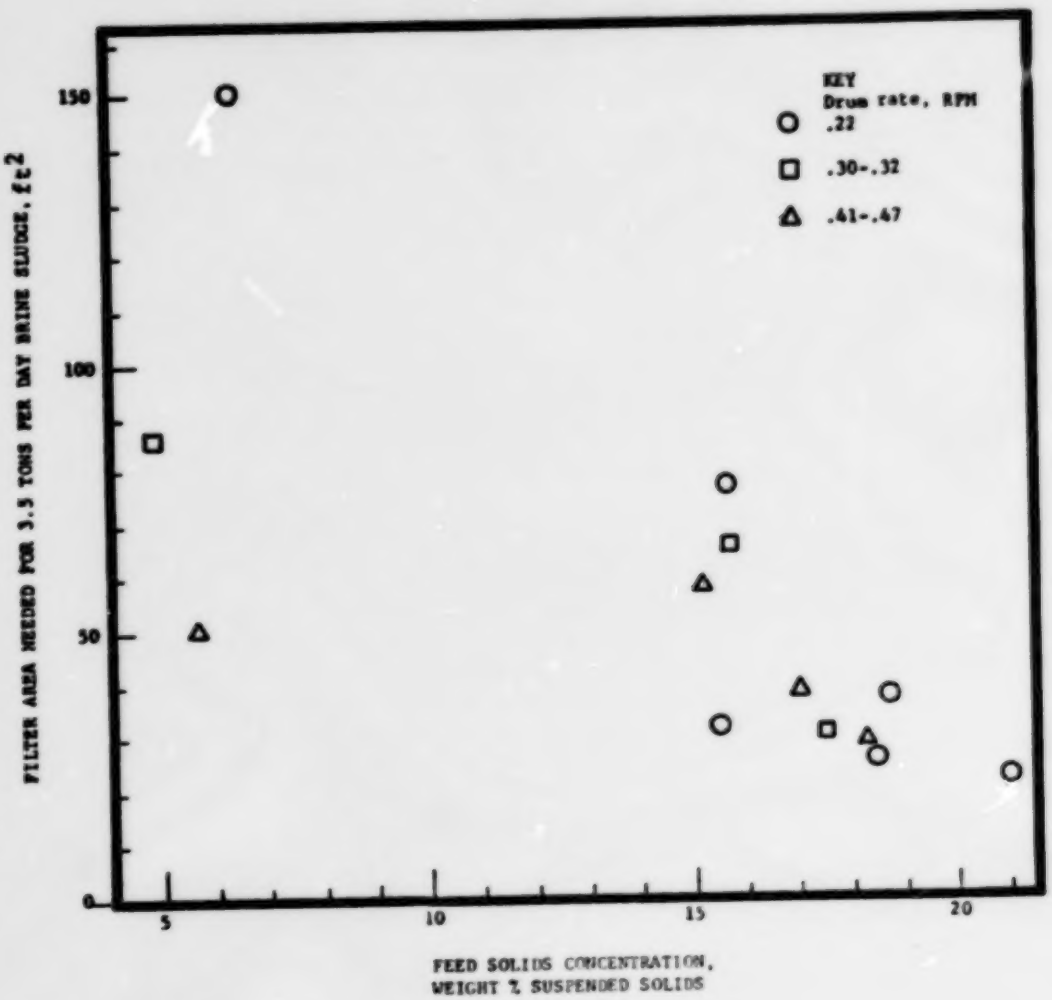


Table 10. DATA FROM THE EIMCO PILOT ROTARY VACUUM FILTER

Test no.	Drum rate, rpm	Feed suspended solids, weight %	Cake dry solids rate kg/hr	Cake dry solids rate lbs/hr	Filter size for 3.5 ton/day m^2	Filter size for 3.5 ton/day sq. ft.	Cake thickness, mm	Cake thickness, in.
1	0.22	18.7	34.2	75.4	3.4	37	5.	0.19
2	0.32	17.6	41.1	90.5	2.9	31	3.	0.13
3	0.41	18.3	44.1	97.3	2.6	28	3.	0.13
4	0.41	17.0	32.3	71.3	3.6	39	3.	0.13
5	0.22	15.5	16.2	35.8	7.2	77	2.4	0.09
6	0.47	15.2	21.5	47.3	5.4	58	1.6	0.06
7	0.30	15.7	19.1	42.0	6.1	66	2.4	0.09
8	0.22	6.3	8.3	18.4	13.9	150	1.6	0.06
9	0.41	5.7	24.3	53.6	4.7	51	1.6	0.06
10	0.30	4.9	16.6	32.1	8.0	86	1.6	0.06
11	0.22	21.0	56.2	124.0	2.0	22	8.	0.08
12	0.22	15.5	38.6	85.0	3.0	32	6.	0.25
13	0.22	18.4	48.5	107.0	2.4	26	4.	0.16

Figure 7. Eimco rotary vacuum pilot filtration of brine sludge



7 m^2 (75 ft^2) was selected. The filters 0.9 m (3 ft) x 2.4 m (8 ft) and 1.8 m (6 ft) diameter x 1.2 m (4 ft) are approximately 7 m^2 (75 ft^2) in area; the larger diameter is preferred since there is greater control of drying time and cake formation time. A 1.8 m (6 ft) x 1.8 m (6 ft) filter would be a good investment since the small additional capital cost would provide 50% more filter capacity in nearly the same space. The filter area would be approximately 10.4 m^2 (112 ft^2). At a filtration rate of 10 - 18 dry $kg/m^2/hr$ (2.3 - 4 dry $lb/ft^2/hr$) with a 33% submergence, the 1.8 m (6 ft) x 1.8 m (6 ft) rotary vacuum filter will discharge 2.8 - 4.9 m tons (6,200 - 10,800 lb) of solids per 24-hour day. The extra capacity permits the filter rpm to be slowed to build a thicker, drier cake if cake discharge becomes a problem.

Equipment Sizing

The system was sized on the basis of 3.2 m tons (3.5 s tons) per day to handle the expected solids from the chlor-alkali plant at a chlorine production of 181 m tons/day (200 s tons/day). This corresponds to a sludge production of 1.37 m tons (1.5 s tons) per day from the plant plus 1.83 m tons (2.0 s tons) per day from stockpiled sludge and other Hg-containing solids.

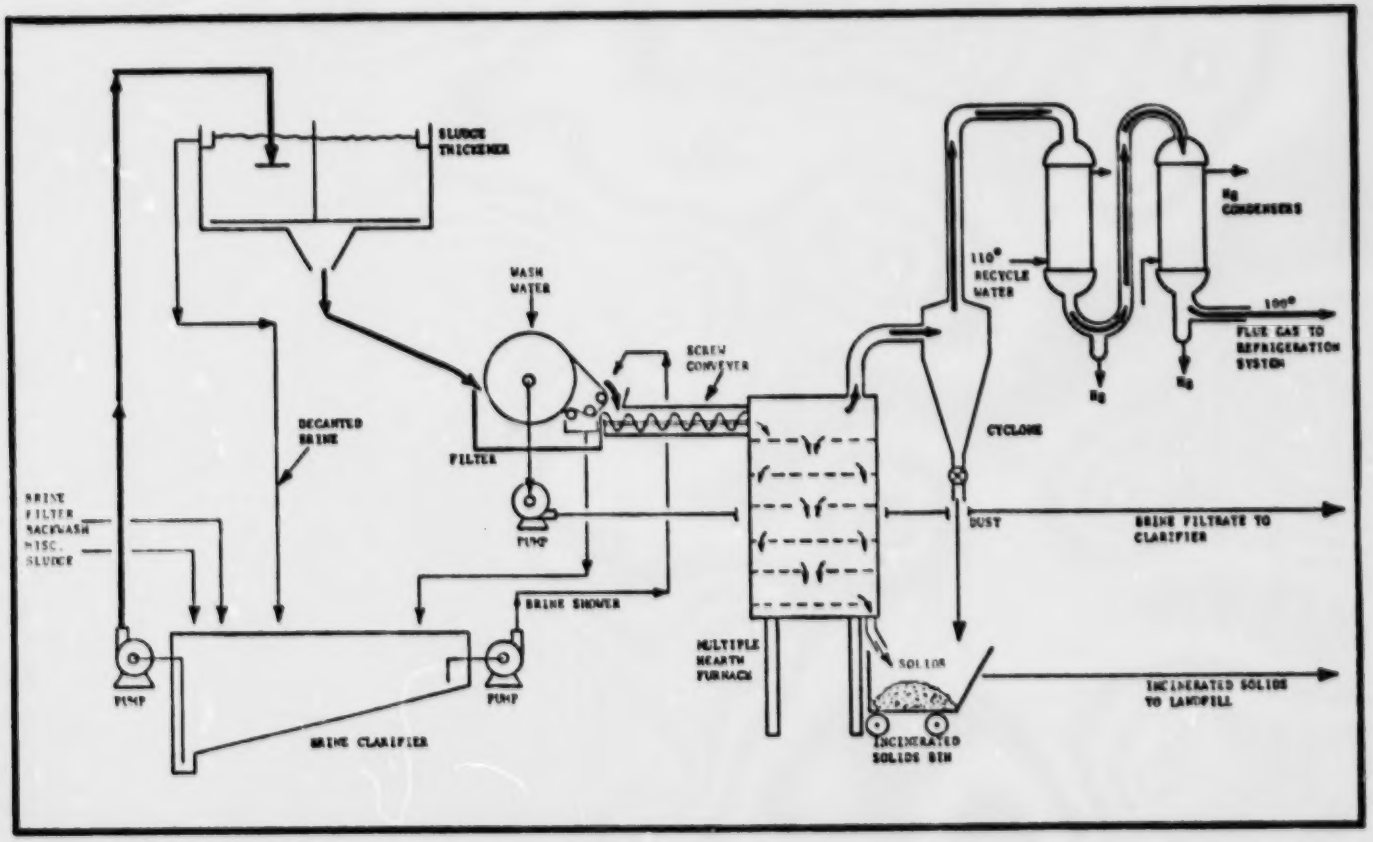
The major pieces of equipment include a 3.7 m (12 ft) diameter x 1.8 m (6 ft) high thickener, a rotary vacuum filter and a 1.37 m (4.5 ft) i.d. 6-hearth multiple hearth furnace (Figure 8). All decanted and filtrate brine is recycled to the settling pond so that the small amounts of solids remaining in these streams will not load up the water handling system. In addition, if shower water is needed to clean the filter cloth or sluice out sludge buildups around the filter, brine will be used and returned to the sludge pit. No fresh water will be used for wash-down to maintain the water balance.

WATER TREATMENT FOR Hg REMOVAL

Laboratory Methods

The test methods used to find the optimum water treatment process involved many standard laboratory procedures. Solid particles such as the ion exchange resins, activated carbons, and metal particles were packed in a glass column of 1.9 cm (3/4 in) i.d. with a packing depth of approximately 30 cm (12 in). A constant liquid flow was maintained by a head of liquid 7.6 cm - 15 cm (3 - 6 in) above the top of the packing. Chemical tests to reduce Hg

Figure 8. Proposed brine sludge handling system



ions with sodium borohydride, to precipitate Hg sulfide with sodium sulfide, or to reduce Hg ions with powdered metals such as zinc or aluminum were performed in 500 ml beakers with magnetic mixer agitation.

The untreated Hg-contaminated water was first added to the beaker. The pH was adjusted with hydrochloric acid or sodium hydroxide to the desired point. The appropriate chemicals were added and mixed for varying periods. The liquid was then filtered through a 10 cm (4 in) or 15 cm (6 in) Buchner funnel precoated with about 6 mm (0.24 in) of diatomaceous earth. The untreated and treated solutions were then analyzed for Hg by flameless AA.

To determine the solubility of mercuric sulfide in solutions of varying pH and excess sulfide, solutions of mercuric chloride and sodium sulfide were combined. The resulting precipitate was collected, washed and weighed into equal amounts. These samples of HgS were placed in sealed containers of water at various pH and excess sulfide, agitated and allowed to come to equilibrium. The supernatant was then analyzed for Hg.

Alternative Methods Investigated

During the laboratory phase of the project, several of the methods proposed for Hg removal from water were tried including:

1. Ajinomoto ion exchange resin
2. Billingsfors - Langed ion exchange resin
3. Nuchar 722 activated carbon
4. Pittsburgh HGR activated carbon
5. Calgon Filtersorb 400 activated carbon
6. Zinc particles
7. Sodium borohydride
8. Stannous chloride

In general, these methods were not able to achieve effluent Hg levels below 0.10 ppm for starting solutions of 2 - 20 ppm, or their capacity was limited so that their effective life was greatly shortened by concentrated Hg feeds. The ion exchange resins and activated carbons ap-

pear to be most effective as polishing steps after the first stage of treatment has removed the bulk of the Hg. They are able to treat solutions in the range of 40 - 100 ppb down to 1 - 5 ppb consistently. Appendix C details the results of these tests.

Using another metal to reduce and adsorb Hg ions while dissolving the second metal tends to trade one effluent problem for another, e.g. the zinc reduction method.

Of the methods tested, sodium borohydride, $NaBH_4$, appears to be the best alternative to the sulfide precipitation for a primary Hg removal process. The equipment necessary is very similar to the sulfide addition process and with careful engineering a system could be built to use $NaBH_4$ - sulfide interchangeably with only minor modifications. The only drawbacks found for the $NaBH_4$ method for this application appeared to be the slightly lower efficiencies found in the lab tests and the higher cost of $NaBH_4$.

Ventron Corporation holds a patent on the use of $NaBH_4$ for heavy metal removal (2).

In the last decade, the literature includes several less common ways to remove Hg from water or brine. Among the methods proposed are: (1) solvent extraction with high molecular-weight amines (3, 4); (2) electrolytic means by passing the solution through a type of diaphragm cell (5, 6); (3) hydroxide flocculation and filtration (7); and (4) adsorption of Hg compounds by CaC_2 slag and flocculation with $FeSO_4$ (8). Of these methods, the latter two seem to have some promise although we did not investigate these techniques.

Sulfide Precipitation

A number of publications have described the use of sulfide ions for precipitation of Hg from water solutions (9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, & 20). It is generally agreed that a removal rate of 99.9% can be achieved with sulfides and this has been confirmed in our test work on laboratory and pilot scales (Table 11).

The drawbacks to this method include: (1) the formation of soluble sulfide complexes at high levels of excess sulfide, (2) the difficulty of monitoring excess sulfide levels, and (3) the problem of sulfide residue in the waste water discharge.

Table 11. LAB TEST DATA ON SULFIDE PRECIPITATION FOR Hg REMOVAL FROM WATER

Sample number	pH	Reaction time, min	Filtration			Acid for pH adjust.	Initial Hg content, ppm	Final Hg, ppm	Hg removal, %
			Filter pad	Precoat	Body feed				
pH Range 7-14									
1	12.0	60				None	4.2	1.8	57.0
2	10.0	60				None	10.0	.36	96.4
pH Range 5-7									
4						HCl	7.0	0.11	98.4
5	5.5	1/2	Paper	D.E.	No	HCl	16.0	0.63	99.6
6	5.5	10	Paper	D.E.	No	HCl	16.0	.04	99.9
7	5.5	60	Paper	D.E.	No	HCl	16.0	.03	99.8
pH Range 1-5									
8	4.5	60	Glass-Fiber	No	No	HCl	52.0	5.6	89.2
9	4.5	60	Glass-Fiber	No	No	HCl	52.0	.44	99.2
10	4.5	60	Glass-Fiber	No	No	HCl	60.0	.03	99.95
11	3.5	60	Glass-Fiber	No	No	HCl	60.0	.02	99.97
12	3.5	60	Glass-Fiber	No	No	HCl	60.0	.01	99.98
13	1.5	120	Glass-Fiber	No	No	HCl	14.0	.18	98.7
14	4.0	30	Glass-Fiber	No	No	HCl	36.0	.002	99.994
15	4.0	60	Glass-Fiber	No	No	HCl	36.0	.015	99.96
16	4.0	60	Glass-Fiber	No	No	HCl	36.0	.006	99.99
17	4.0	50	Glass-Fiber	No	No	HCl	36.0	.002	99.994
18	1.0	60	Glass-Fiber	No	No	HCl	36.0	.012	99.96
19	3.0	60	Glass-Fiber	No	No	HCl	10.0	.008	99.92
20	4.0	60	Glass-Fiber	No	No	HCl	10.7	.12	98.9
21	4.0	20	Paper	D.E.	D.E.	HCl	27.0	.31	98.8
22	4.5	30	Paper	D.E.	D.E.	H_2SO_4	17.5	.15	99.1
23	4.5	30	Paper	D.E.	D.E.	HCl	17.5	.1	99.4

From our work we have found that sulfide excess is less critical so long as the HgS precipitate is filtered out of the solution as soon as it is formed, as shown in Table 12.

Table 12. HG LEVELS IN WATER AFTER EXPOSURE TO SULFIDE ION FOR 30 SECONDS TO 10 MINUTES

	Mercury content of solution, ppb	Exposure time to sulfide ion, min	Hg removal, %
Starting solution	51,500	0	----
After precipitation & filtration	9.7	0.5	99.98
	15.0	2.0	99.97
	15.0	5.0	99.97
	14.0	10.0	99.97

Probably the sulfide comlex is formed more slowly than the mercuric sulfide particle.

$$Hg^{\circ} + Hg_2^{+2} + Hg^{+2} + 2S^{-2} \underset{\longleftarrow}{\xrightarrow{\text{rapid}}} 2HgS + 2Hg^{\circ}$$

$$HgS + S^{-2}\ (\text{excess}) \underset{\longleftarrow}{\xrightarrow{\text{slower}}} HgS_2^{-2}$$

In laboratory sulfide precipitation tests, 99.98% of the Hg was reacted after only 30 seconds of contact. For all practicle purposes, the reaction can be said to go to completion in 30 - 60 seconds. As Figure 9 indicates, even large excesses of sulfides did not reduce the recovery of Hg significantly. Therefore, the accurate monitoring of the excess sulfide level is not necessary.

The third problem stated above, that of sulfides discharged with the treated water, is easily solved in a chlorine plant. There is normally a small amount of residual chlorine in the main cooling water stream which effectively oxidizes the sulfide ion. If residual chlorine is not available in the treated discharge, then

a small amount of sodium or calcium hypochlorite can be added to the filtered waste water to eliminate the remaining sulfide ion.

The most critical parameter in controlling the sulfide precipitation of Hg was found to be pH. Lab tests were performed using mercuric sulfide which was precipitated from mercuric chloride and sodium sulfide solutions (Figure 9). A standard solution of sodium sulfide was prepared and placed in full bottles of water containing various concentrations of sodium sulfide. The mixtures were agitated several times and then allowed to settle 24 - 48 hours, enough time for the Hg in the solid phase to approach equilibrium with the Hg in solution. The results appear in Figure 9 as initial excess sulfide level versus final dissolved Hg level as a function of starting pH.

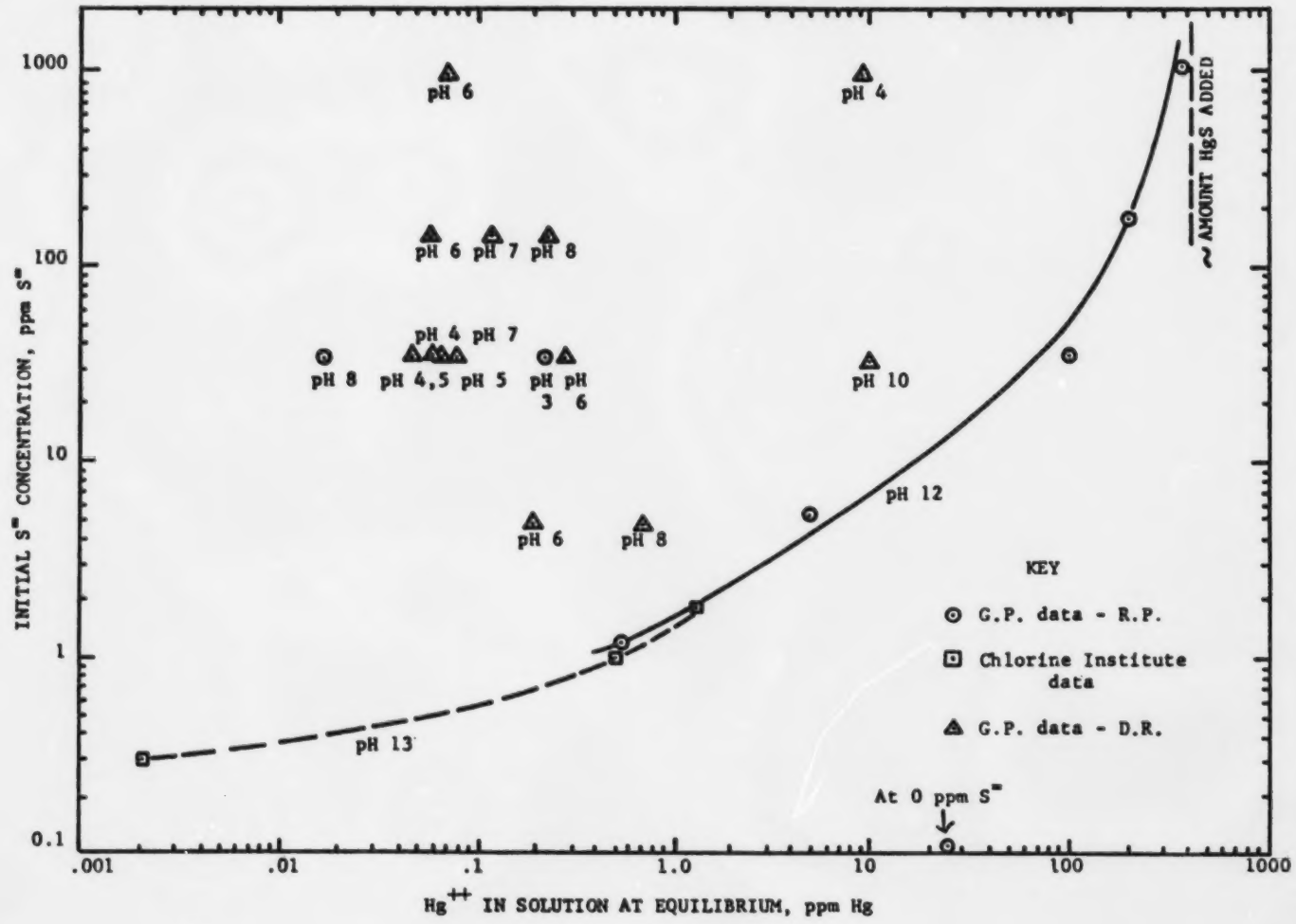
Since this experiment allowed a lengthy contact time, it is likely that the soluble mercuric sulfide ions, $HgS_2^{=}$, are formed at the higher initial sulfide levels so that high dissolved Hg levels are due to both pH and excess sulfide.

From the data presented, it appears that within the pH range of 3 - 8 the level of excess sulfides does not affect the amount of Hg sulfide which is redissolved. Less than 0.1% of the mercuric sulfide added to the sulfide containing water redissolved at these pH conditions in 48 hours. However, as high as 75% of the mercuric sulfide redissolved above a pH of 10.

Possible methods of adding a controlled amount of sulfide to the waste water stream are: (1) meter the desired concentration from a concentrated NaHS solution, (2) add the solid NaHS or Na_2S particles from a dry feeder, or (3) pass the waste water through a bed of less toxic metal sulfide which has the proper solubility to release sulfides at the 1 - 5 ppm level.

The first method has been used exclusively in our test work because it is the easiest in batch tests in the lab or pilot plant. However, on a continuous plant scale the second method would eliminate the need for an operator to mix an exact solution concentration. Instead, he could simply add a bag or two of the solid sulfide to the dry feeder hopper when necessary. A possible problem with this method is the rate of dissolution of the sulfide particles in the cold waste water. If sufficient agitation and residence time were not provided, the sulfide would not dissolve completely.

Figure 9. Solubility of HgS in excess $S^{=}$



The third method proposed has been discussed but not tested. In theory, since a certain excess sulfide must be maintained, it should be possible to control this excess chemically. By finding a sulfide compound of the correct solubility and forming a packed bed of this material, the waste water passing through the bed would pick up the metal and sulfide ions to saturation. As the sulfide ions are consumed in the HgS precipitate, more sulfide would dissolve according to the solubility product of the specific metal sulfide used. Possible problems with this method are: (1) toxicity of the metal ion selected, (2) coating or deactivation of the bed by contaminants in the waste water, or (3) suppression of the solubility of the metal sulfide if the metal ion concentration is high in the waste water.

The Selected Water Treatment Process

Of the alternatives considered, it appeared that the sulfide precipitation method was the best choice for several reasons. First, only five processing steps are needed to achieve 99% Hg removal. These steps are: pH adjustment to 5 - 7, addition of the sulfide ion, addition of the filter aid, filtration, and solids feed to the furnace. Most other methods require 1 - 3 more steps (figures 10 - 13).

Secondly, the pH adjustment which is required of the waste water changes the pH slightly to the acidic side which will help to neutralize the basic cooling water effluent. Thirdly, the precipitated Hg is in a very concentrated form in the filter cake, 15 - 30% Hg, and can be fed into the furnace without adding significantly to the solids load. Finally, the sodium sulfide is inexpensive and no additional contaminating ions will be in the effluent after the excess sulfides are eliminated by available chlorine in the remaining effluent.

The process proposed is shown in figures 13 & 14. The process begins with the collection of all the Hg contaminated waste water in a 170,000 l (45,000 gal) agitated tank. The pH is adjusted in this tank automatically and continuously by the addition of spent sulfuric acid from pH 11 down to pH 5 - 6. The waste water flows from this vessel into a container in which the concentrated sodium sulfide solution (or sodium hydrosulfide solution) is added by a metering pump. The treated waste water is then pumped through a system which adds a measured amount of filter aid, diatomaceous earth, to the stream. It then flows through a pressure filter which separates the Hg-bearing solids from the water. The solids are discharged in a slurry and pumped into the sludge dewatering filter.

Figure 10. Schematic of the reduction method of Hg removal from water

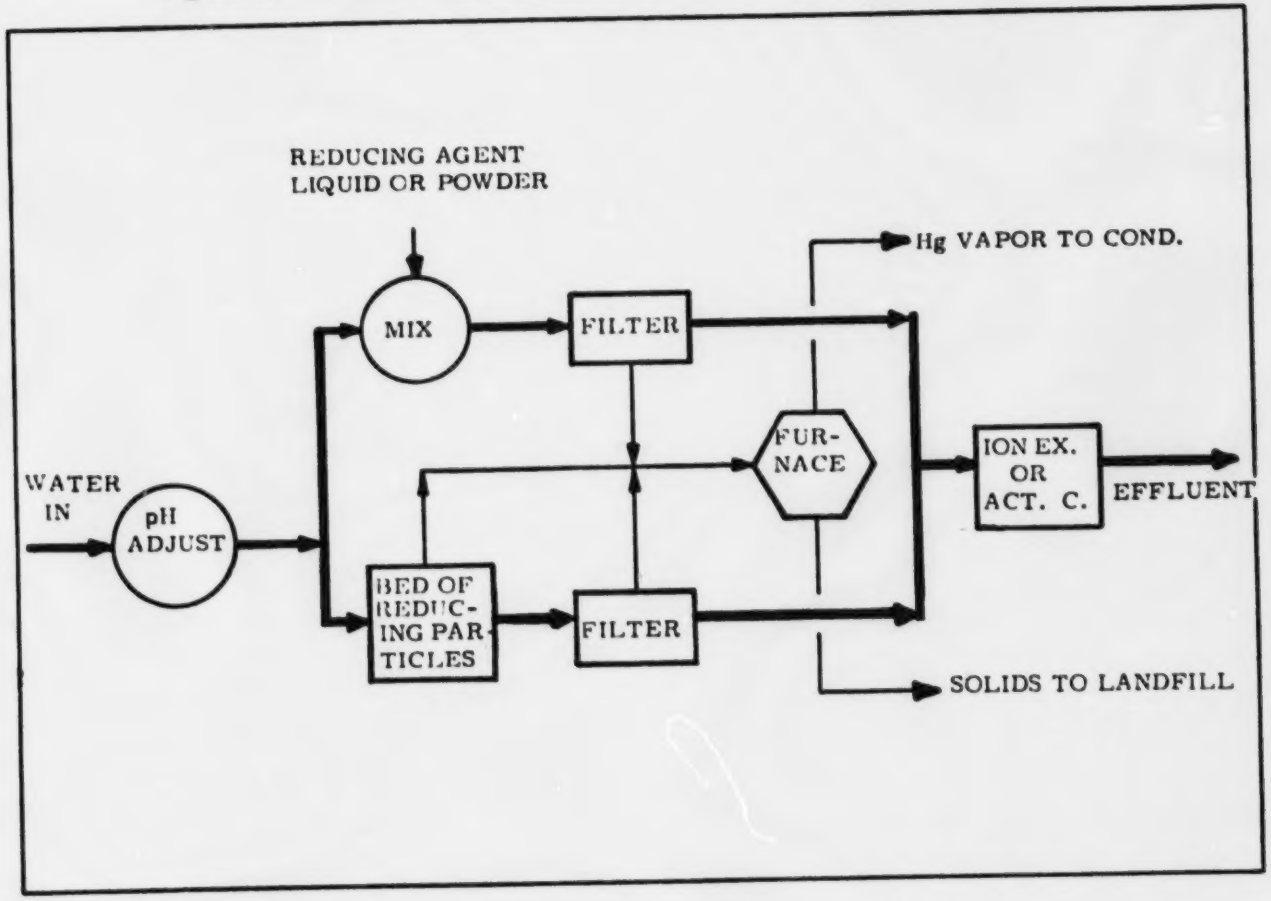
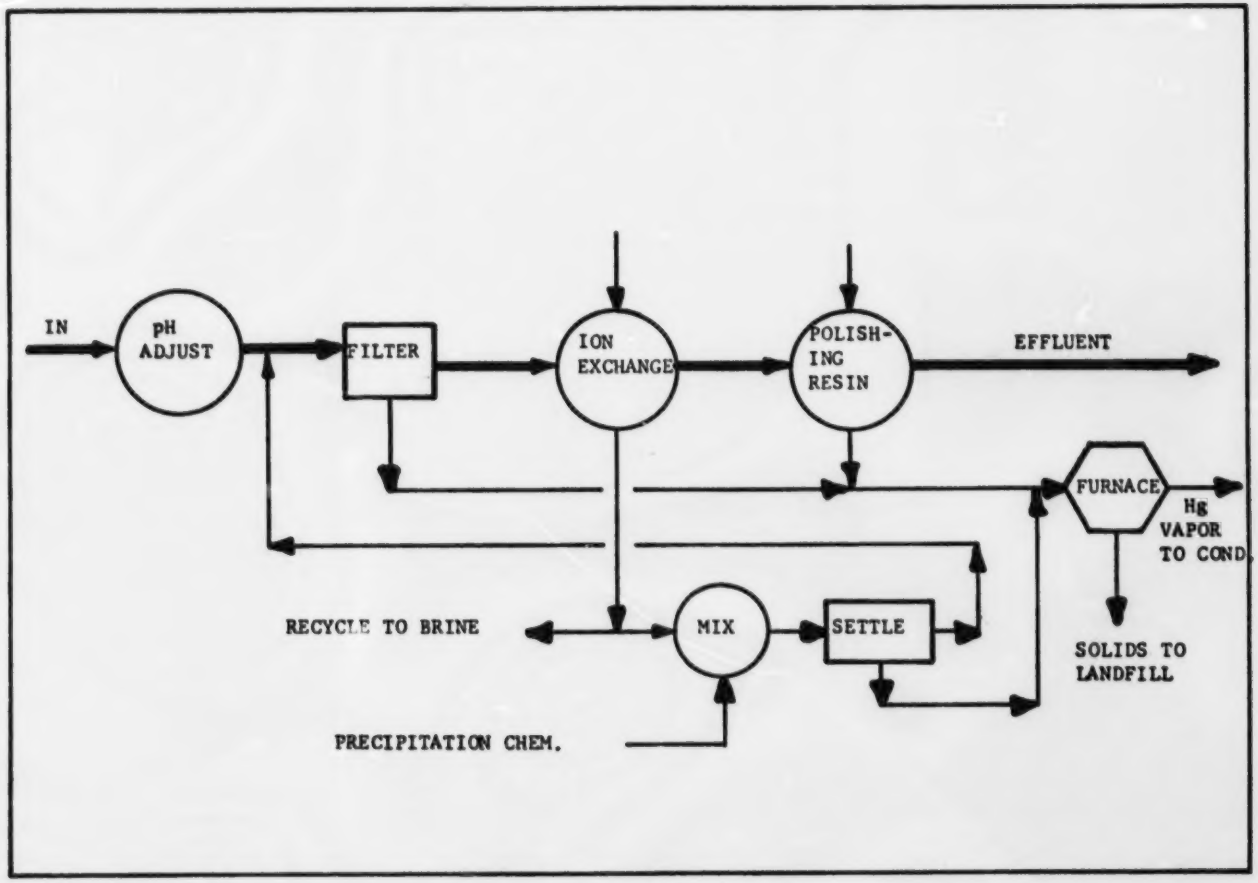


Figure 11. Schematic of the ion exchange process for Hg removal from water



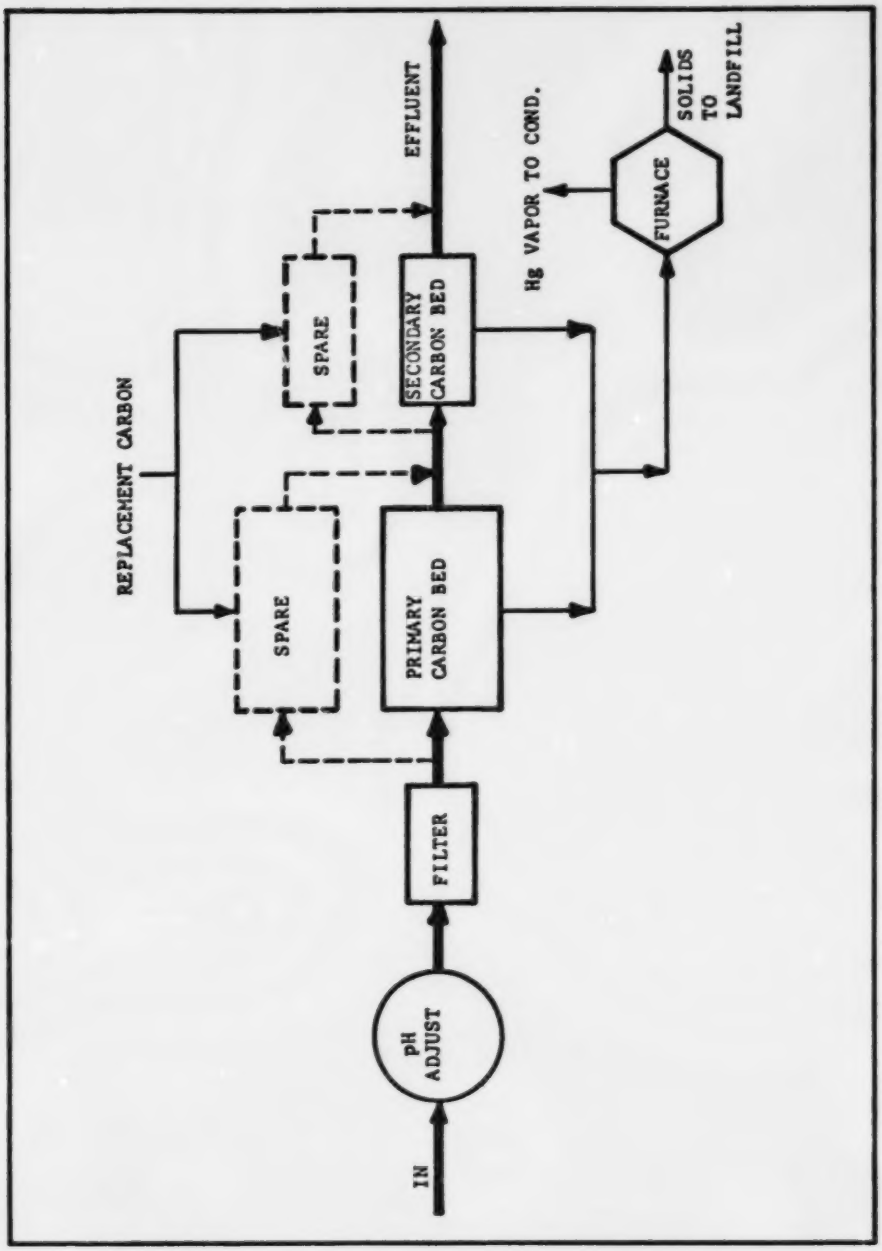


Figure 12. Schematic of activated carbon Hg removal from waste water

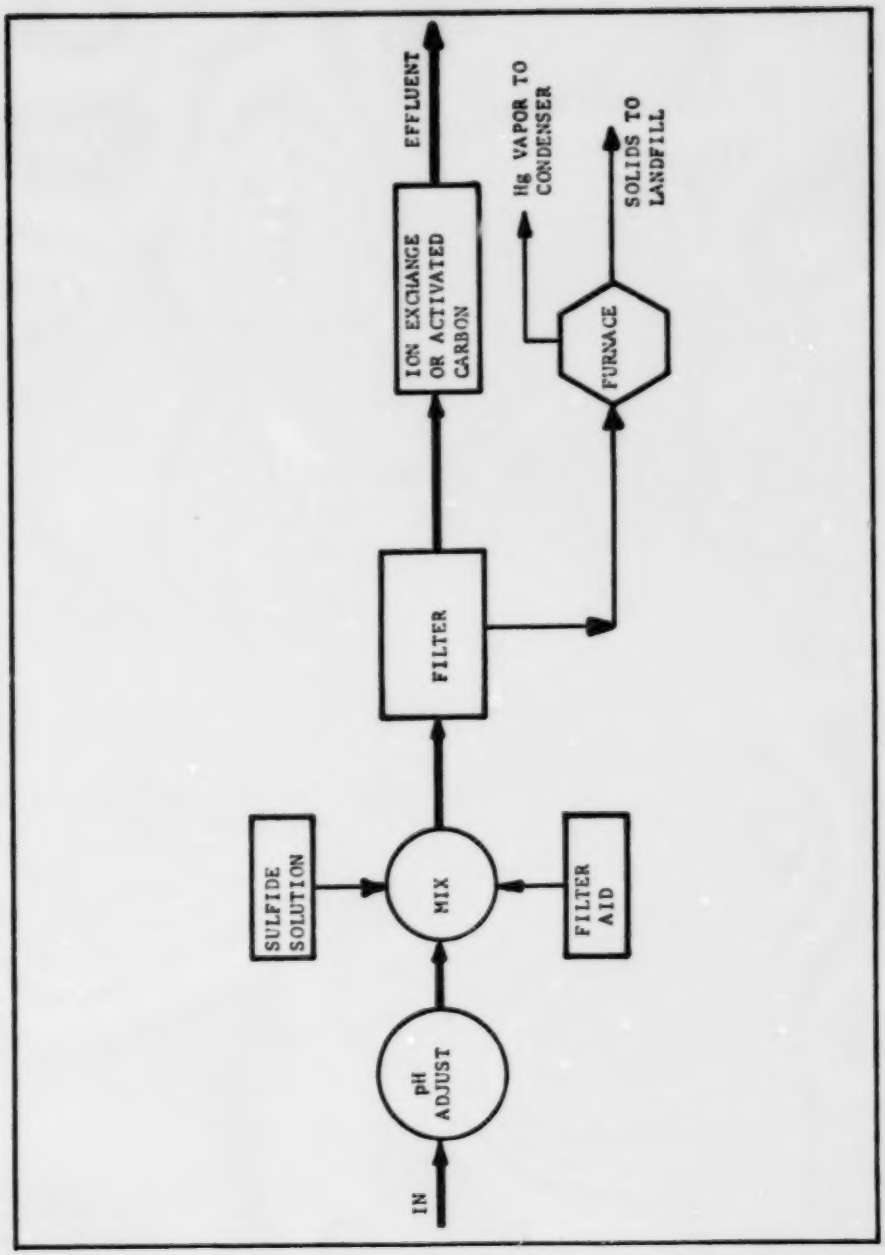


Figure 13. Schematic of the sulfide precipitation process for waste water

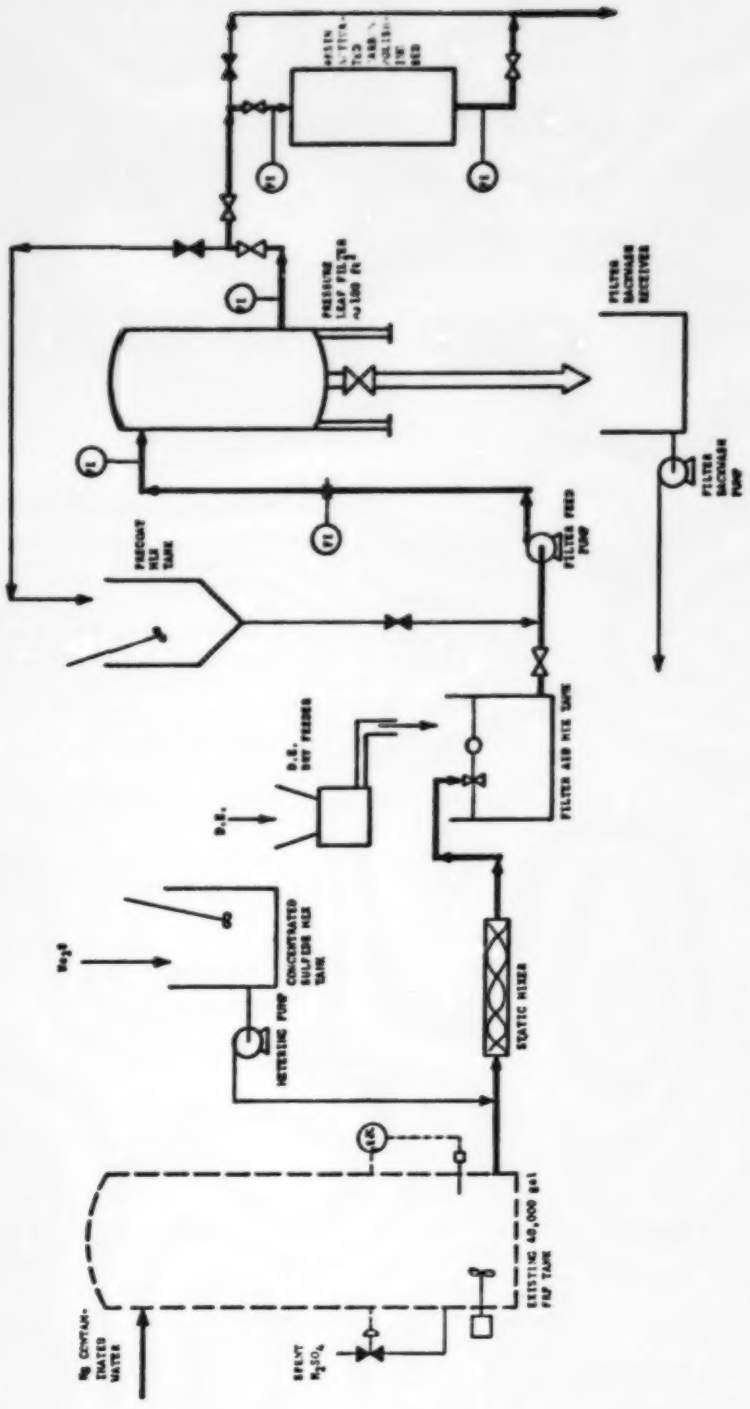


Figure 14. Proposed sulfide precipitation system

The filtered water might then either go to the outfall or pass through an optional activated carbon or resin bed for a final polishing step before discharge.

Liquid/Solid Separation Techniques

This liquid-solids separation consists of removing 22 kg (60 lb) per day of fine particles from a 150,000 l (40,000 gal) water stream. Thus, the solids make up 0.02% by weight of the liquid stream or < 0.01% by volume. A pressure filter is normally used, since centrifuges handle high solids loading, rotary vacuum filters handle medium solids loading, and pressure filters normally handle the solids loading below 10% solids by volume.

A number of alternatives were evaluated:

1. Dry or slurry solids discharge?
2. If dry discharge, vibrating or centrifugal action cake removal?
3. Should the filtering elements be vertical cylinders, vertical plates or horizontal plates?
4. Should a precoat be added and what type?
5. Is continuous filter aid addition necessary?
6. Should the entire chamber open or one large bottom outlet be provided?

In selecting the proper filter, the method of cake removal is the most important feature to be examined. Almost any filter will build up a suitable cake; the problem is frequently to remove the cake completely and restore the original clear filtering area (21).

It is desirable for further handling of the Hg-containing cake that the driest cake possible be discharged from the filter. However, because of the small solids loading, 22 kg (60 lb) per day, the difficulty of cleaning the filter properly without washing, and the extra cost involved for the more complex equipment, $5,000 - $10,000 additional for a 9 m^2 (100 ft^2) filter, we believe the sluicing and settling technique is best for this application.

It is more difficult to sluice clean a horizontal filter. Also, filtration occurs only on one side of the horizontal leaf whereas both sides of a vertical are available for filtration, producing a smaller filter for the same total area. For these reasons a vertical cylinder filter was selected.

For the efficient filtration of fine Hg sulfide particles, a precoat is advisable. Our pilot runs on a batch pressure filter with horizontal leaves showed that diatomaceous earth, cellulose fibers and activated carbon are all effective at removing the Hg sulfide, although the diatomaceous earth was slightly more effective (Figure 15). Since the Hg sulfide particles are so fine, they tend to form an impervious layer on the filtration media rather rapidly. However, the addition of small amounts of diatomaceous earth as a filter aid continuously to filter feed water extended the cycle time by a factor of 10 - 20. The diatomaceous earth was added at the rate of 0.7 gpl (Figure 16).

The diatomaceous earth filter aid and Hg sulfide will continue to build up on the filter elements until the cake space between elements is full. It is preferable to backwash the filter before the cake volume is completely full for a more complete cleaning action.

Figure 15. Data from pilot tests with 11 sq. ft. Niagara filter

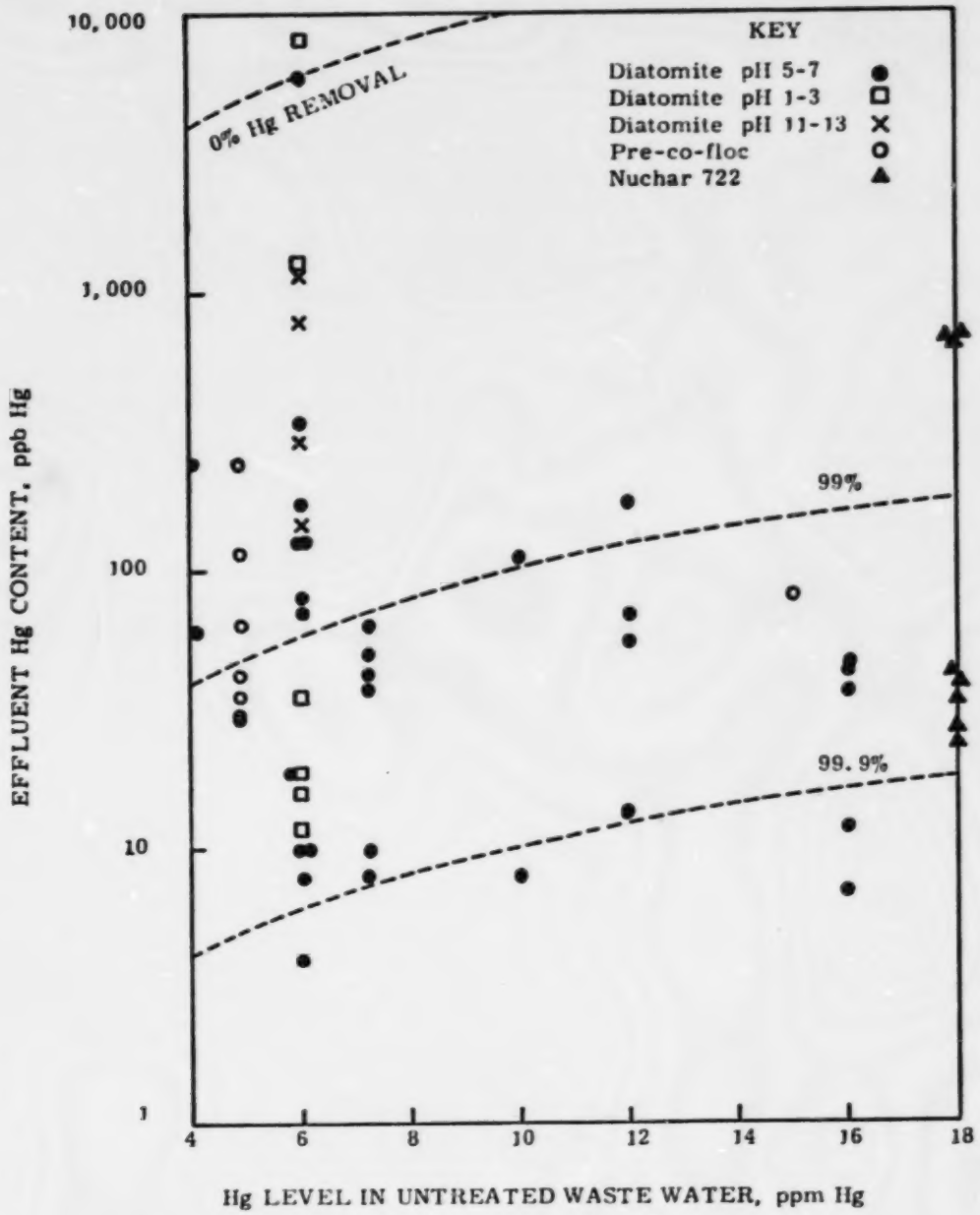
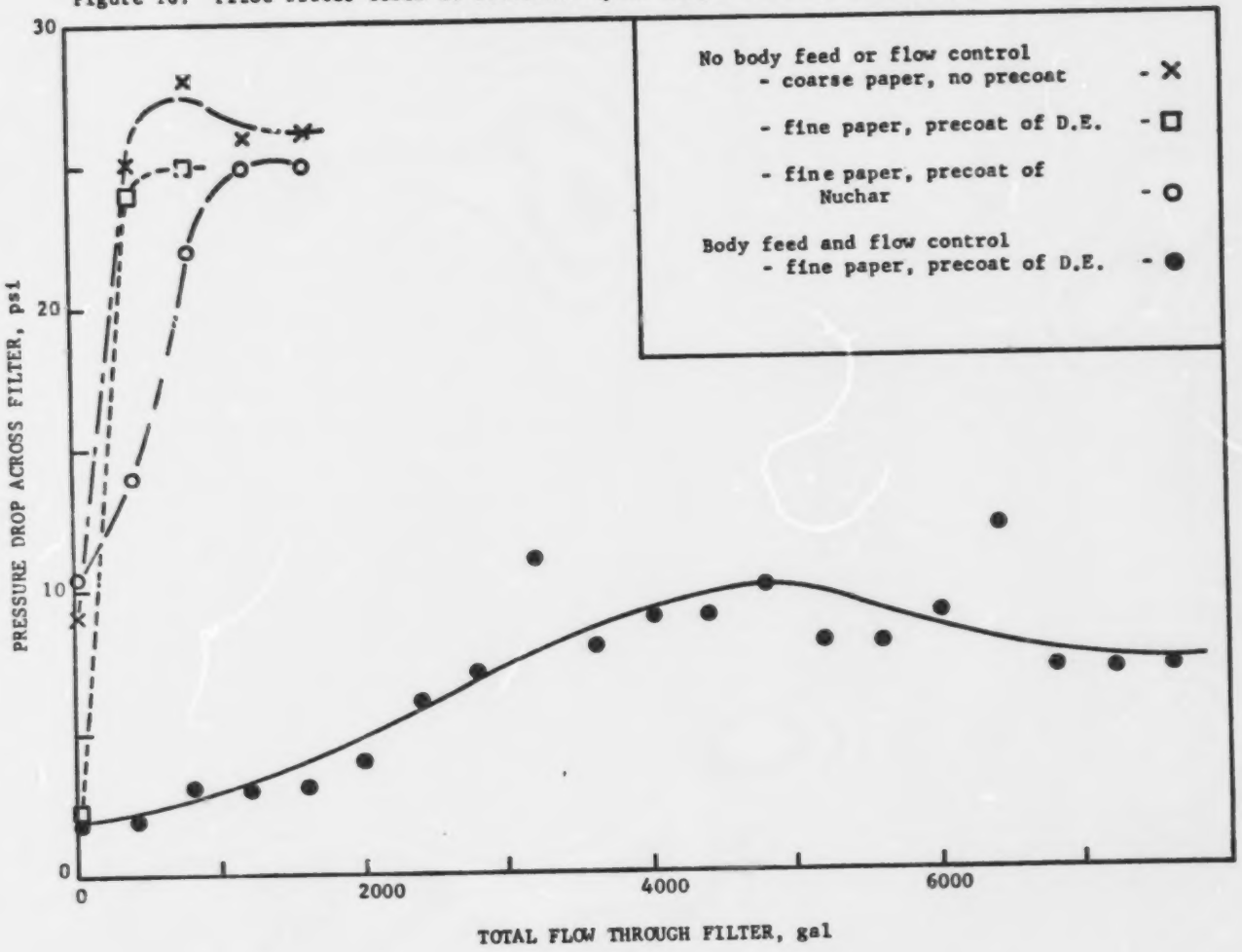


Figure 16. Pilot filter tests to determine cycle length with and without precoast and body feed



SECTION V

CONSTRUCTION

PROCEDURE

Following the selection of sulfide precipitation for water treatment and sludge roasting for solids treatment, the construction phase of the project began in October, 1972. Construction consisted of several phases:

1. Selection and ordering of long delivery time items.
2. Design and construction of the supporting structure.
3. Installation of major pieces of equipment.
4. Process piping.
5. Supplying of necessary utilities.
6. System start-up and modifications.

The equipment ordering began in October, 1972; construction began in March, 1973. Start-up of the water treatment system began November, 1973, and start-up of the sludge system began in January, 1974.

Selection of Major Equipment

The longest delivery time item appeared to be the multiple hearth furnace with a 32-week delivery. Three suppliers were investigated: MSI Industries, Envirotech, and Nichols Engineering. Envirotech was selected on the basis of equipment quality and personnel experience in Hg ore roasting.

The rotary vacuum filter was the other major piece of equipment in the sludge system and the alternative manufacturers of plastic or rubber-lined rotary vacuum filters for corrosive liquids were Ametek and Eimco. The Eimco unit was selected because a one-month old unit of all plastic construction wa. available at reduced cost with immediate delivery.

The only long delivery time item for the water treatment system was the pressure filter. There are a large number of domestic and foreign manufacturers of pressure filters in various designs. The manufacturers investigated were:

1. Buffalo Filters
2. De Laval
3. Durco - Enzinger
4. Niagara Filters
5. R. P. Adams
6. U. S. Filters
7. Votator - Schenck

The R. P. Adams filter was selected based on: (1) operator and maintenance experience with this model, (2) standardization of parts with existing filters, (3) ease of cake removal with few moving parts, and (4) price per square meter of filter area.

Construction Model

In order to assist in arranging the equipment for this project, a student engineer was assigned the task of constructing a model of the entire system (Figure 17). Due to the solids handling problems, the elevations and equipment and piping layouts were critical.

The model was also useful during the operator training phase of the project. Before the construction was complete the operators could see the location of the pipes and valves during the training classes.

Modifications During Construction and Start-up

Originally, the design called for an anode crusher and conveyor to process the spent cell anodes. However, during the project, the decision was made to convert over to metal anodes so the anode crusher was eliminated.

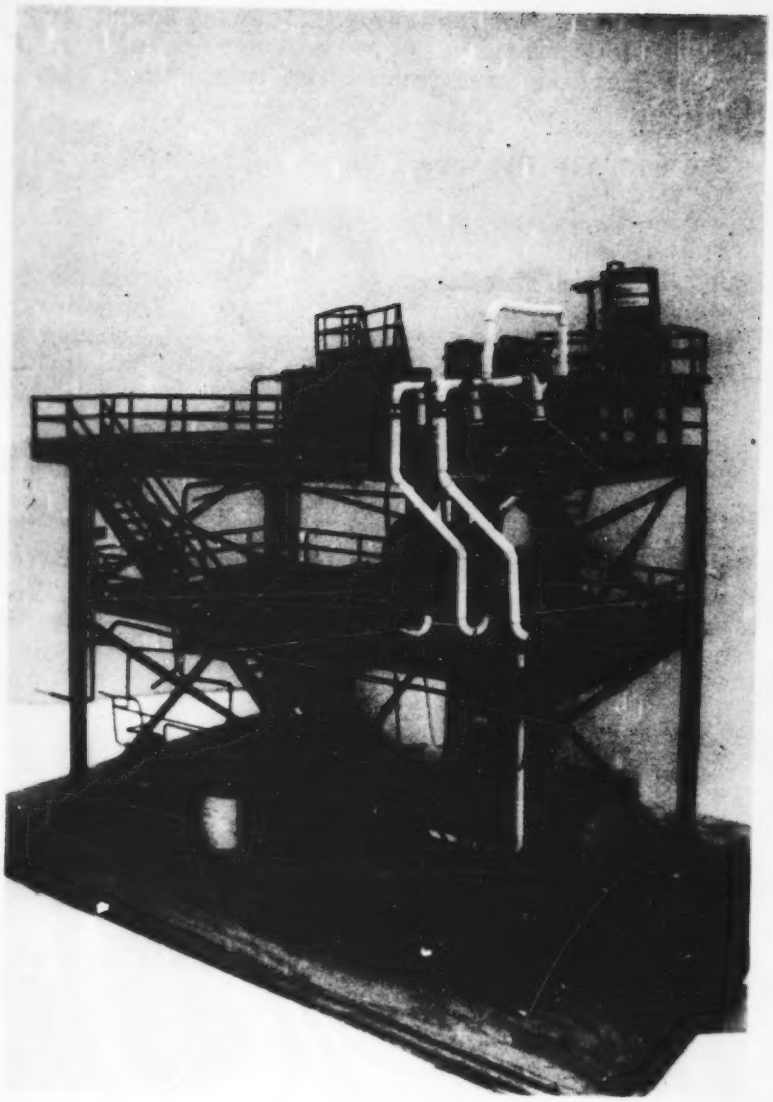


Figure 17. The model of the Hg Recovery System

Between the plant sludge collection system and the rotary vacuum filter it was planned to have batch settlers. However, since the other equipment was continuous, the batch settlers were replaced with a continuous thickener. In practice the thickener is not needed since the sludge is fed in batches from it anyway.

SECTION VI

OPERATION AND EVALUATION

START-UP OF WATER SYSTEM

Objective

Following the construction stage, the start-up crew began checking out the individual parts of the water treatment process and training the operators. This phase began in mid December, 1973 for the water treatment part of the project. The goal was to reduce the chlorine plant effluent to less than 45 g (0.1 lb) Hg per day by January 1, 1974, in compliance with discharge permit T-3456, and have the bugs worked out of the system.

Start-up

The start-up phase of the water treatment system lasted approximately one month, from mid December, 1973 to mid January, 1974 before control was turned over to the operators. The major changes to the original design were: (1) rerouting of the Hg-containing water through the pond, (2) changes in the acid addition system, and (3) a change in the sulfide storage and addition mechanisms.

Untreated water flow from the cell room was intermittent, from a collection sump. This made pH adjustment difficult. Therefore, the existing pond was used as a surge tank to give a constant flow to the pH adjustment system. The acid addition system was also modified to provide two-stage dilution for pH adjustment of the waste water with concentrated spent sulfuric acid. At present, the system controls in the range of 6 - 8 pH.

Originally, the sodium sulfide was to be mixed in a storage tank and then transferred to a small metering tank to be metered into the process through a pump. This was altered so that the sulfide flows directly from the large storage tank to the mix tank through a rotameter.

Evaluation

At present, the water treatment system is operating as expected and requires approximately 30 - 45 minutes of operator time each shift. Following the initial shakedown period, the operators seem pleased with the

system. The only operator attention needed normally is to add diatomaceous earth once per shift and backwash once every 1 - 2 days.

From a design viewpoint, the system is operating as desired. The 50 ppb average effluent from the system at an average flow of 150 l/min (40 gpm) accounts for only 20% of the maximum allowable 45 g (0.1 lb) per day Hg discharged. The Hg in the filter cake is fed back to the sludge system as a slurry after each backwash for disposal by incineration. As shown in Table 13, the average Hg removal has been 97% the first 3 months of operation and the effluent Hg content has averaged 49 ppb.

START-UP OF SLUDGE SYSTEM

Objective

As the construction neared completion, the start-up crew began checking out each piece of equipment by moving the sludge through each stage of the process. As expected, the main problems encountered in this start-up were solids handling. The start-up began in early March, 1974 and the operators took over two months later.

Problems Encountered In Start-up

The majority of changes in the sludge system during start-up were in the conveying system between the rotary vacuum filter and the furnace. Originally a Moyno pump was installed, but when the cake was dry enough to discharge well from the filter, 65% total solids, the cake was too dry for the Moyno pump to handle. Next, a screw conveyor was tried but it was still necessary to add a little water to the filter cake to keep it from sticking to the screw. Finally, a small belt conveyor was installed which appears to be working well. At present, a 5-vane star valve is being tested as an air seal where the sludge enters the top of the furnace. The sludge did not plug this star valve in the one-hour tests run to date.

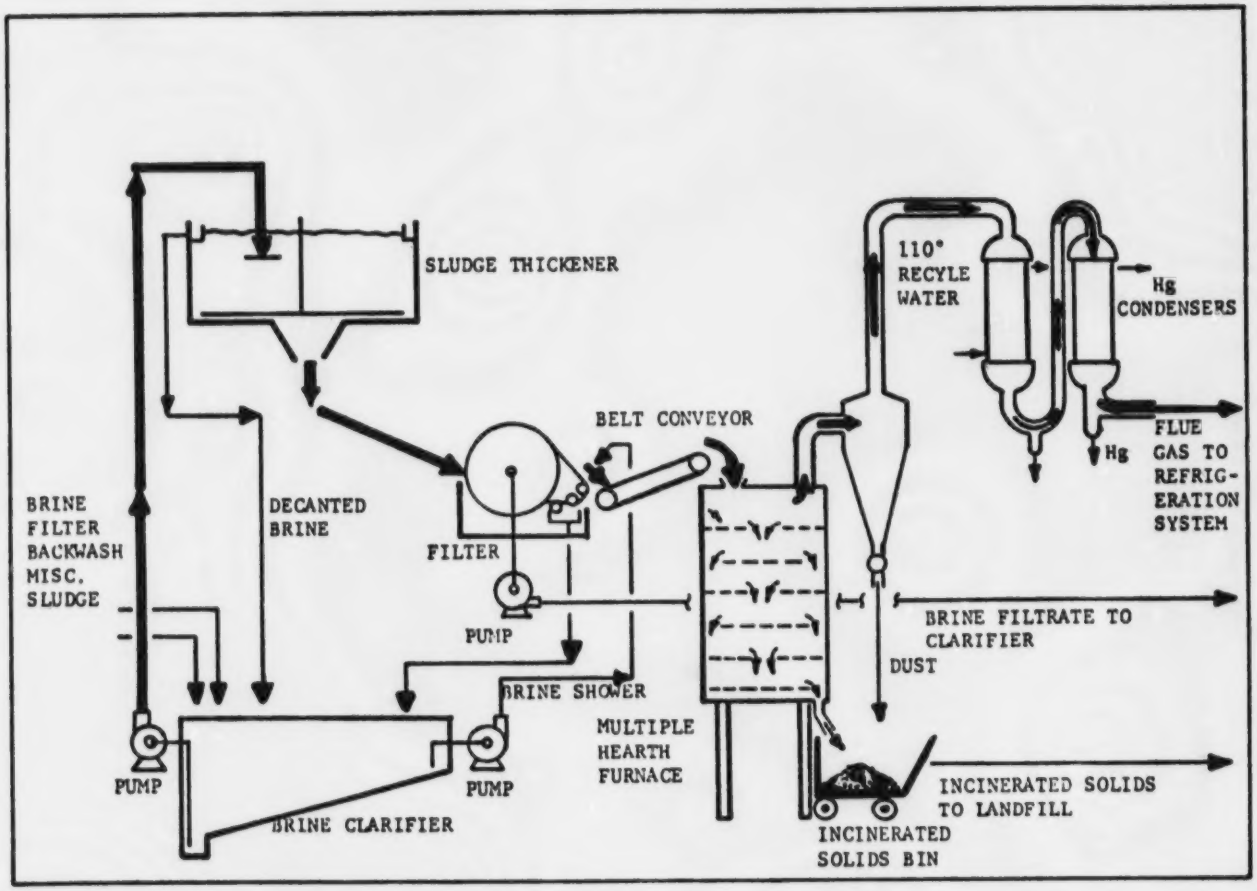
Other changes have been made during the operation to improve the system (Figure 18). It was found that a large number of sticks were being pumped out of the clarifier and plugging the line to the thickener. Therefore, the strainer was moved from just before the thickener to just after the clarifier. A flow indicator was also installed in the line to the thickener so that the operators could readily tell when this flow stops for any reason.

Table 13. PARTIAL LIST OF DATA FROM START-UP OF FULL SCALE SULFIDE PRECIPITATION SYSTEM

Date	Hg content, ppb Feed	Filtrate	% removal	pH	Excess Na_2S, ppm	Flow rate l/min.	gpm
12-9-73	820	16	98.0	6.5	2	330	85
12-9-73	740	40	94.5	6.2	2	310	80
1-2-74	2000	48	97.6	5.8	2	330	85
1-8-74	1400	125	91.0	8.0	0	310	80
1-9-74	1400	50	96.4	7.6	1	310	80
1-15-74	140	18	87.1	5.9	-	388	100
1-23-74	800	42	94.7	6.0	2	290	75
3-12-74	5000	68	98.6	6.9	2	310	80
3-15-74	1300	96	92.6	6.8	-	310	80
3-20-74	6000	50	99.2	7.2	-	310	80
3-26-74	5800	51	99.1	6.0	-	330	85
Average*		49 ppb	96.8%				
Minimum:	300	10	87	5.1	0	290	75
Max.	6000	125	99.2	8.2	3	388	100

* The average values for 30 sets of data

Figure 18. Installed brine sludge handling system



Due to the small size and plugging potential of the control valve between the thickener and the rotary vacuum filter, the small continuous valve was replaced with a larger intermittent valve. Rather than holding the filter at a constant level, it is allowed to cycle over a 7.6 - 10 cm (3 - 4 in.) range.

The rotary vacuum filter was able to pick up a thicker cake 6 - 10 mm (1/4 - 3/8 in.) than was found in our pilot tests. As a result, the drive sprocket on the rotary vacuum filter was reduced in size so as not to overload the furnace. The Eimco rotary vacuum filter minimum rotation speed was reduced from one revolution in 14 minutes to one revolution in 26 minutes. The filter apparently has ample capacity for future needs.

Evaluation

At present, from a design standpoint, the system is working better than expected. It runs consistently at a feed rate of 6.4 m tons (7 s tons) of sludge per 24 hours and will remove 99.8% of the Hg from the sludge at 730°C - 760°C (1350°F - 1400°F). The system operates with a feed content of 345 ppm Hg and a discharge (clinker) Hg content of 0.5 - 0.8 ppm (Table 14). This feed rate is twice the design rate. As a result of the high throughput, lower sludge output from plant than expected, and no return of sludge from the pond to date, it is only necessary to operate the furnace 1 or 2 shifts every 3 days. At other times, the temperature is lowered to 370°C - 480°C (700°F - 900°F) to reduce refractory stress. As lower quality salt is processed, producing more sludge, and as sludge inventory is reprocessed, the filter and furnace will operate for longer periods.

From furnace tests, it has been found that dredged material from bark sludge beds can only be fed at about one half the rate of brine sludge through the furnace because of its different handling characteristics. Therefore, the furnace capacity drops to 3.5 m tons (3.8 s tons) per day for dredged cellulosic material.

From an operator's standpoint, the process is working well at this stage. The biggest problems seem to be plugging of the strainer between the clarifier and thickener, and conveying problems between filter and furnace. The wood problem in the strainer may be eased by

Table 14. DATA FROM START-UP OF THE FULL SCALE BRINE SLUDGE TREATMENT SYSTEM

Sludge Source	Addition rate kg/hr	Addition rate lb/hr	Temperature °F	Temperature °C	Hg ppm, Feed	Hg ppm, Clinker	% removal Range	% removal Avg.
Brine Sludge	226	540	1400	760	345	0.5-0.8	99.8	99.8
" "	255	560	1250	677	255	1.6-3.1	98.7-99.2	
" "	264	580	1350	732	290	1.7-2.6	99.1-99.4	
" "	205	450	1350	732	438	2-7.2	98.3-99.5	98.9
" "	309	680	1386	752	370	1.6	99.6	
Bay dredging	137	300	1350	732	128	0.95-1.7	86.7-92.1	

more careful wood removal by the screens in the brine flow ahead of the clarifier. The sludge conveying problem into the furnace is being solved by the start-up and construction crews as problems appear.

The Hg recovery from the air leaving the furnace still requires modification to solve the dust plugging problem in the condensers. At present the condensers must be cleaned every 2 - 7 days.

The air leaving the condensers has been analyzed to contain approximately 0.5 lb Hg per day. The stream is routed to an existing chilled water heat exchanger and a Brink demister for Hg recovery. This recovery system recovers over 90% of the mercury.

SECTION VII

DISCUSSION

DESCRIPTION AND ANALYSIS OF WORK PERFORMED

Literature Search and Company Contacts

At the beginning of the project, an extensive literature survey was conducted utilizing the Chemical Abstracts, the Dow Chemical Company Keyword Index on Environmental Aspects of Mercury Usage, and others (22, 23, 24, 25). Pertinent articles from various periodicals and patents were collected for study. Also, 22 organizations in or associated with the chlor-alkali industry, were contacted by phone, mail, or in person to gather information on the methods used or contemplated for Hg removal from solids and liquids. These contacts are listed in Table 15.

Laboratory Tests, Process Design & Equipment Selection

As discussed in Section IV, a series of laboratory and pilot tests were conducted on brine sludge to learn which method was the most effective and practicle to scale up to a full size plant. Of the methods tried, sludge roasting resulted in the lowest Hg in the clinker by 2 - 3 orders of magnitude.

Concurrently with the sludge trials, tests were performed in the laboratory on Hg contaminated waste water to select a process capable of removing Hg to meet the January 1, 1974 limit of 45 g (0.1 lb) per day maximum Hg discharged in the water effluent. The literature survey revealed a large number of alternate water treatment methods tried, proposed, or potentially effective. Several samples of ion exchange resins and activated carbons claimed to remove Hg from water were purchased.

As the data show (tables 11, 16, 17, 18, 19 and Figure 19) a large number of tests were performed varying the parameters of concentration, reaction or residence time, pH and filtration methods. In addition to resins and carbons, reducing agents (both metallic and chemical), sulfide ion precipitation, and flocculating agents were tried. The most consistently effective and practical method from these experiments was a combination pH adjustment and sulfide precipitation followed immediately by filtration on a precoated filter.

Table 15. NAMES AND ADDRESSES OF THE COMPANIES CONTACTED FOR INFORMATION BY DIRECT COMMUNICATION DURING THE PROJECT

Company name	Address
a) Aktiebolaget Billingsfors-Långed	S-660 11 Billingsfors Sweden
b) FMC Corporation	Squamish, B. C. Canada
c) Weyerhaeuser Company	Chlorine Plant P. O. Box 188 Longview, Wash. 98632
d) Stauffer Chemical	Axis, Alabama 36505
e) Chemapec, Inc.	1 Newark Street Hoboken, N. J. 07030
f) Crawford & Russell, Inc.	Stamford, Conn. 06904
g) Rohm and Haas Company	Ion Exchange Dept. Independence Mall West Philadelphia, Penn. 19105
h) Sobin Chlor-Alkali, Inc.	P. O. Box 149 Orrington, Maine 04474
i) Ventron Corporation	Congress Street Beverly, Mass. 01915
j) Hoechst-Uhde Corporation	550 Sylvan Avenue Englewood Cliffs New Jersey 07632
k) Diamond Shamrock	Deer Partk, Texas 77536

Table 15. CONT.

Company name	Address
l) Wyandotte Chemical Corp.	P. O. Box 161 Port Edwards, Wisc. 54469
m) B. F. Goodrich Chemical Co.	P. O. Box 527 Calvart City, Kentucky 42029
n) Monsanto Company	Sanget, Illinois 62201
o) British Petroleum (BP) Chemicals	Murgatroyd's Works Sandbach, Cheshire
p) Mo Och Domsjo	Husum, Sweden and Örnskoldsvik, Sweden
q) Finnish Chemicals Oy	Äetsa, Finland

Table 16. DATA FROM LITERATURE ON ION EXCHANGE RESINS

Literature source	Initial Hg level, ppb	Hg level after this series of tests, ppb		
		Pre-filtration	I. E. resin	Polishing resin
(5) Osaka Soda process	~20,000	~5,000	150	2-5
(18) Dow Chemical patent #3,083,079	15,000	None	300	
(28) A. B. Billingsfors - Langed	2,000-5,000	None	100-200	10-20
(41) Terraneers process (ion exchange or adsorbant material not specified)	29,000-70,000	None	110-1500	
(62) Ajinomoto Co. of N.Y.	1,000-15,000	Yes Not measured	1-10	

Table 17. LAB TEST DATA ON ION EXCHANGE RESIN FOR Hg REMOVAL FROM WATER

Resin Company	pH	Initial Hg, ppm	Final Hg, ppm	Hg removal, %
Ajinomoto	11	13.5	0.38	97.2
Ajinomoto	11	1.8	.99	45.0
Ajinomoto	1.5	.06	.005	92.0
Ajinomoto	6.0	.087	.003	96.5
Ajinomoto	1.5	189.00	1.9	99.0
Ajinomoto	6.0	205.00	0.4	99.8
Billingsfors-Langed	11	13.5	1.8	86.7
Billingsfors-Langed	11	1.8	2.0	0
Billingsfors-Langed	1.5	189.00	51.5	63
Billingsfors-Langed	6.0	205.00	15	92.7
Billingsfors-Langed	6.5	0.035	.001	97.0

NOTE: All tests were performed in a glass column 3/4" i.d. with a packing depth of 12 inches. Flow was controlled by maintaining a head of liquid 3-6" above top of packing.

Table 18. LAB TEST DATA ON ACTIVATED CARBON FOR Hg REMOVAL FROM WATER

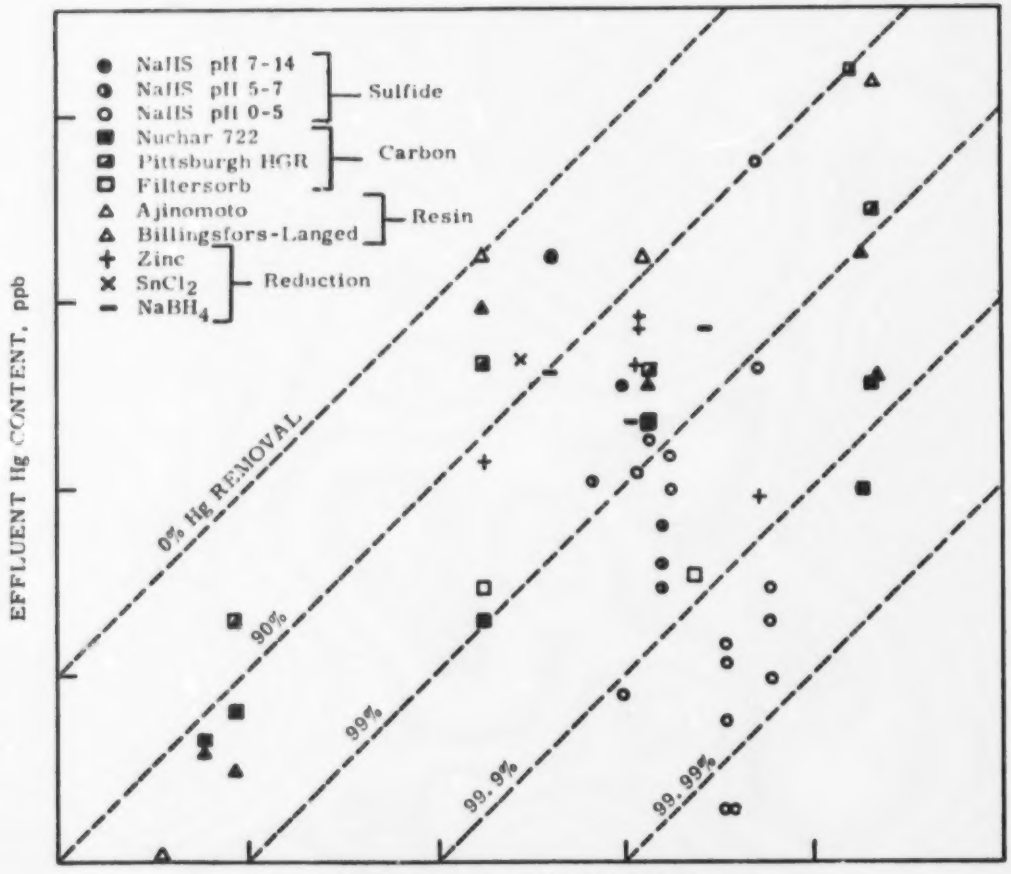
Activated Carbon	Initial pH	Initial Hg, ppm	Final Hg, ppm	Hg removal, %
Nuchar 722	11.5	13.5	0.23	98.3
Nuchar 722	11.5	1.8	.02	98.9
Nuchar 722	6.0	.087	.006	93.0
Nuchar 722	1.5	.060	.0045	92.5
Nuchar 722	6.0	205	.37	99.8
Nuchar 722	1.5	189	.1	99.95
Pittsburgh HGR	11.5	13.5	0.43	96.8
Pittsburgh HGR	11.5	1.8	.47	73.9
Pittsburgh HGR	6.0	.087	.020	77.0
Pittsburgh HGR	6.0	205	3.1	98.5
Pittsburgh HGR	1.5	189	16	92.0
Calgon Filtersorb 400	11.5	13.5	0.73	94.6
Calgon Filtersorb 400	11.5	1.8	.03	98.3

NOTE: All tests were performed in a glass column 3/4" I.D. with a packing depth of 12 inches. Flow was controlled by maintaining a head of liquid 3-6" above top of packing.

Table 19. LAB TEST DATA ON Hg REMOVAL FROM WATER BY REDUCTION

Reduction agent	Material form	pH	Initial Hg, ppm	Final Hg, ppm	Hg removed, %
Zinc particles	10 mesh	11.5	1.8	0.14	92.2
		10.0	12.5	.83	93.4
		6.0	12.5	.75	94.0
		2.5	12.5	.47	96.2
		6.2	52.0	0.09	99.83
Sodium borohydride	Liquid	12.2	10.7	0.22	98.0
		----	4.0	.42	89.5
		----	26.0	.82	96.85
$SnCl_2$	Solution	----	2.8	.5	82.0

Figure 19. Lab tests on mercury removal from water using sulfide ppt., activated carbon, ion exchange resins and reduction chemicals



Following the selection of the water and sludge treatment processes, the preliminary process design was drawn up and cost estimates made (figures 8 and 14). During the interval between the preliminary process design and full scale plant start-up, there were several equipment and process changes. The system in operation is essentially that shown in figures 18 and 20.

The major pieces of equipment consisted of a filter and furnace in the sludge system and a filter in the water system. Due to the need for nearly complete solids removal from the water phase and the high solids content, vacuum filtration was selected (Figure 21).

A number of different furnace designs were considered but this was narrowed to two basic designs for pilot tests due to temperature limits and solids handling problems. Tests were conducted on a rotary calciner, indirect fired and on a multiple hearth furnace (MHF), direct fired. The multiple hearth furnace was selected because it produced lower Hg levels in the clinker (Figure 22).

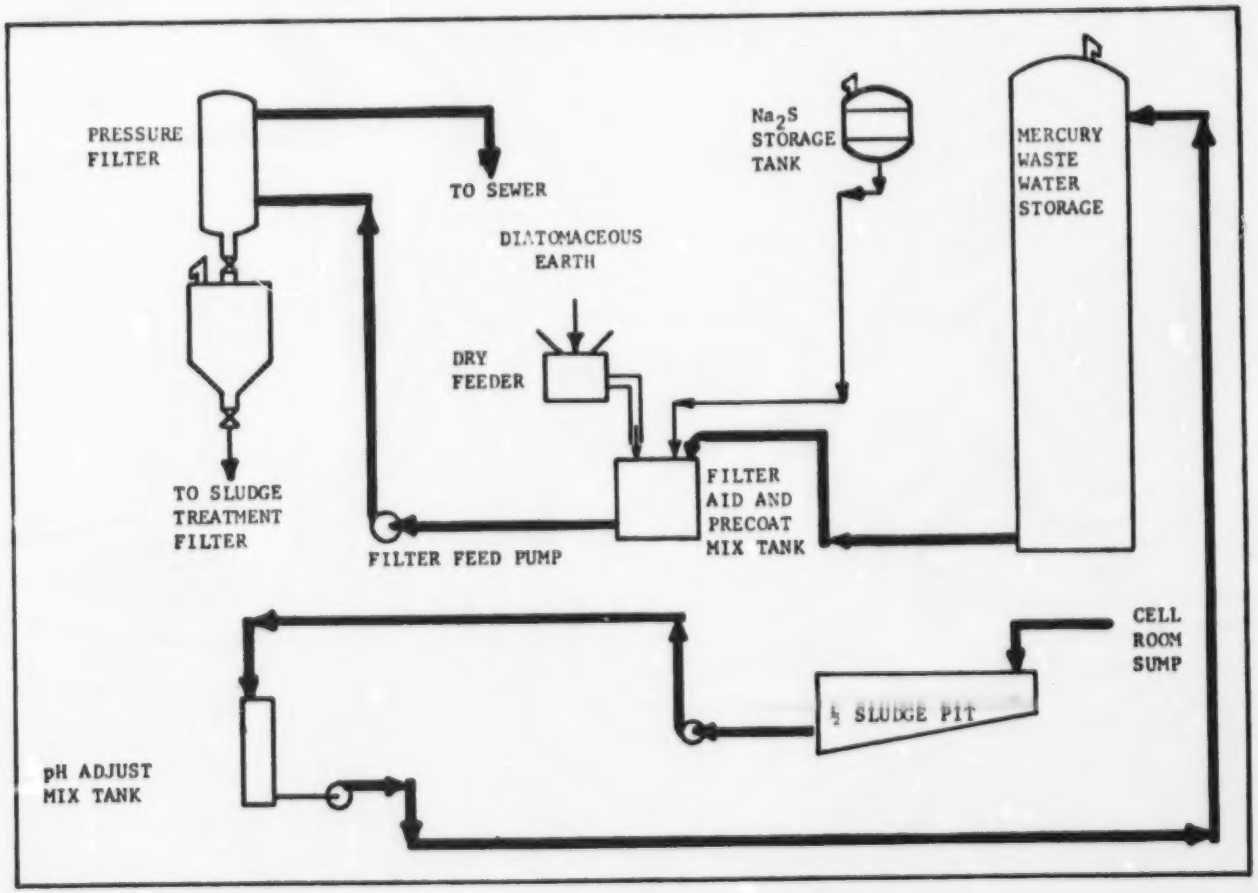
The filter in the sulfide precipitation system called for a type that would remove a small amount of fine solids from a water stream with minimum losses. This narrowed the filter selection to a pressure filter and probably a precoated pressure filter due to the fine particle size (Figure 23).

Construction

As equipment selection was made the first stages of construction took place. Engineering drawings and a plant model (Figure 17) were made. The support structure and foundation were designed and construction was started. As the major pieces of equipment arrived they were installed. The multiple hearth furnace is shown in Figure 22, the rotary vacuum filter in Figure 21, the R. P. Adams filter in Figure 23, and the sludge thickener in Figure 24.

Once the major equipment, pumps and various tanks were in place, the piping was laid by the contractor and the electrical contractor was called in to wire the process. A separate contractor was hired to design and install the instrumentation for the multiple hearth furnace. One major piece of construction involved piping the natural gas from the nearest location to the furnace, a distance of 350 m (1150 ft).

Figure 20. Installed sulfide precipitation system for water treatment



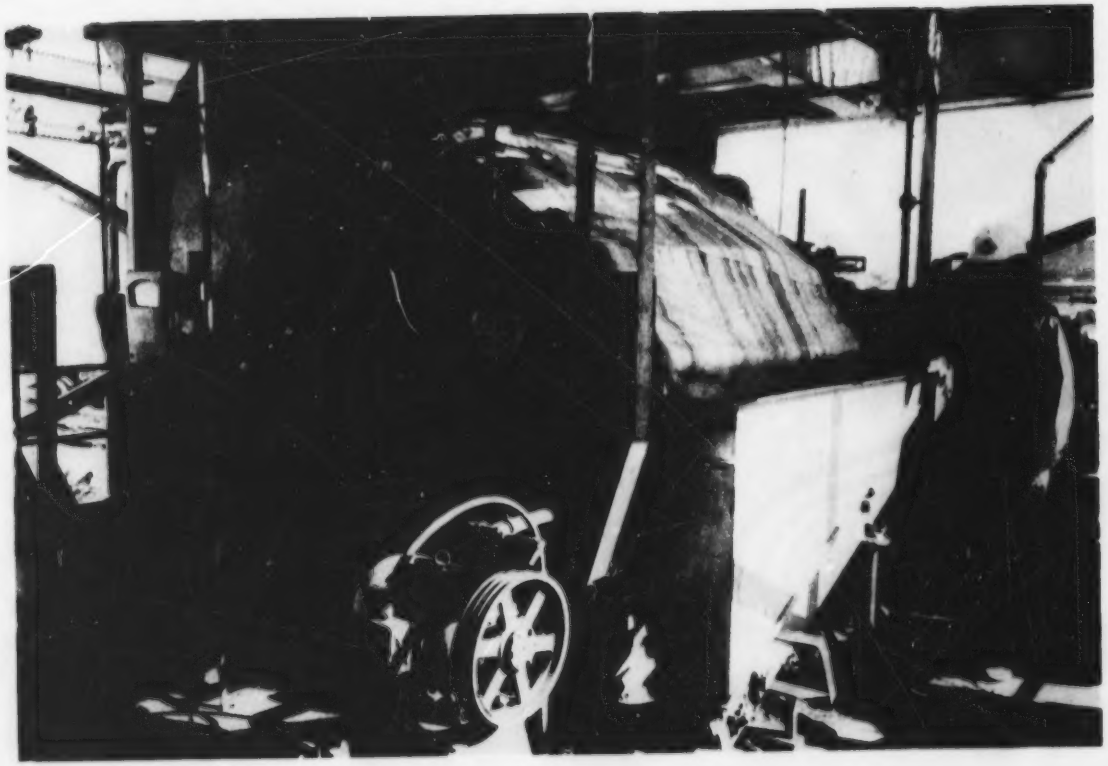


Figure 21. Installed 6' x 6' Eimco rotary vacuum filter for brine sludge dewatering

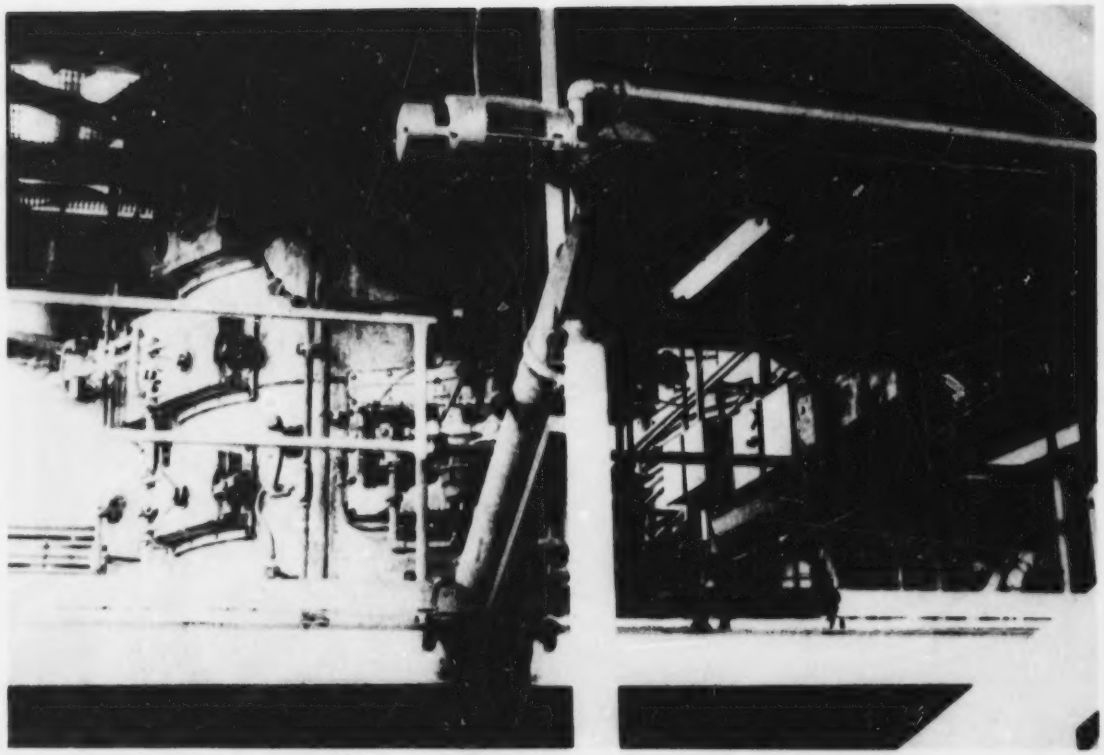


Figure 22. Installed 54" i.d. BSP multiple hearth furnace

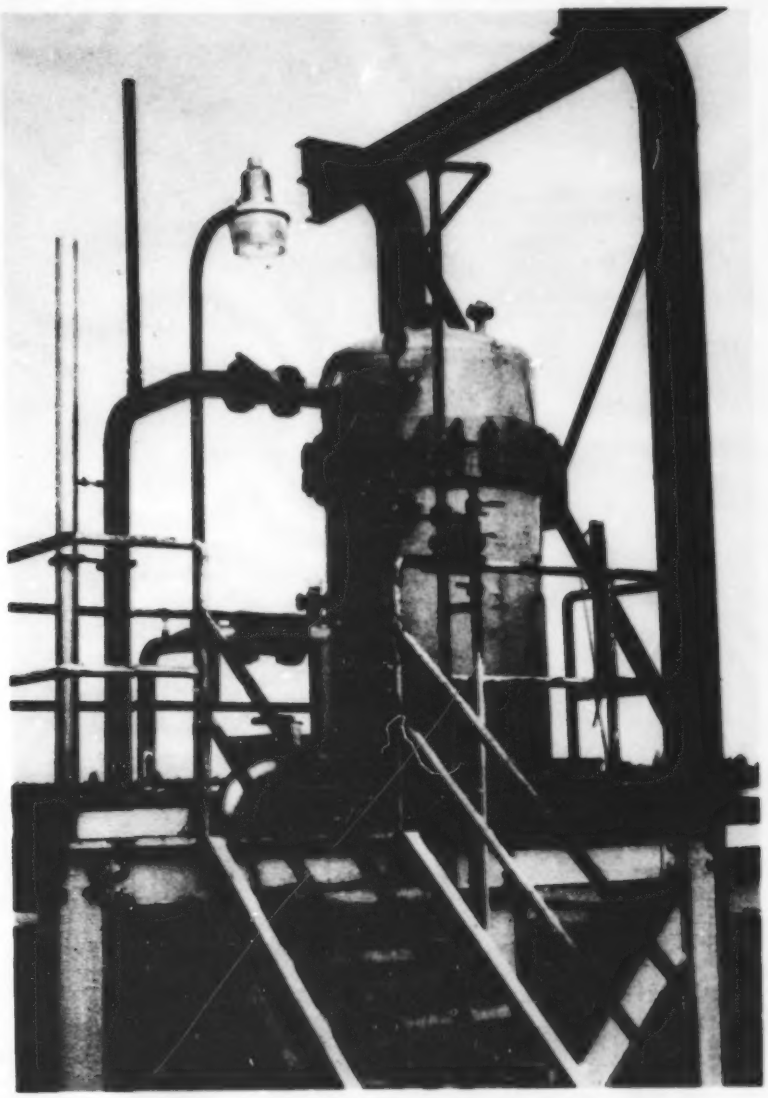


Figure 23. Installed R. P. Adams filter for HgS removal

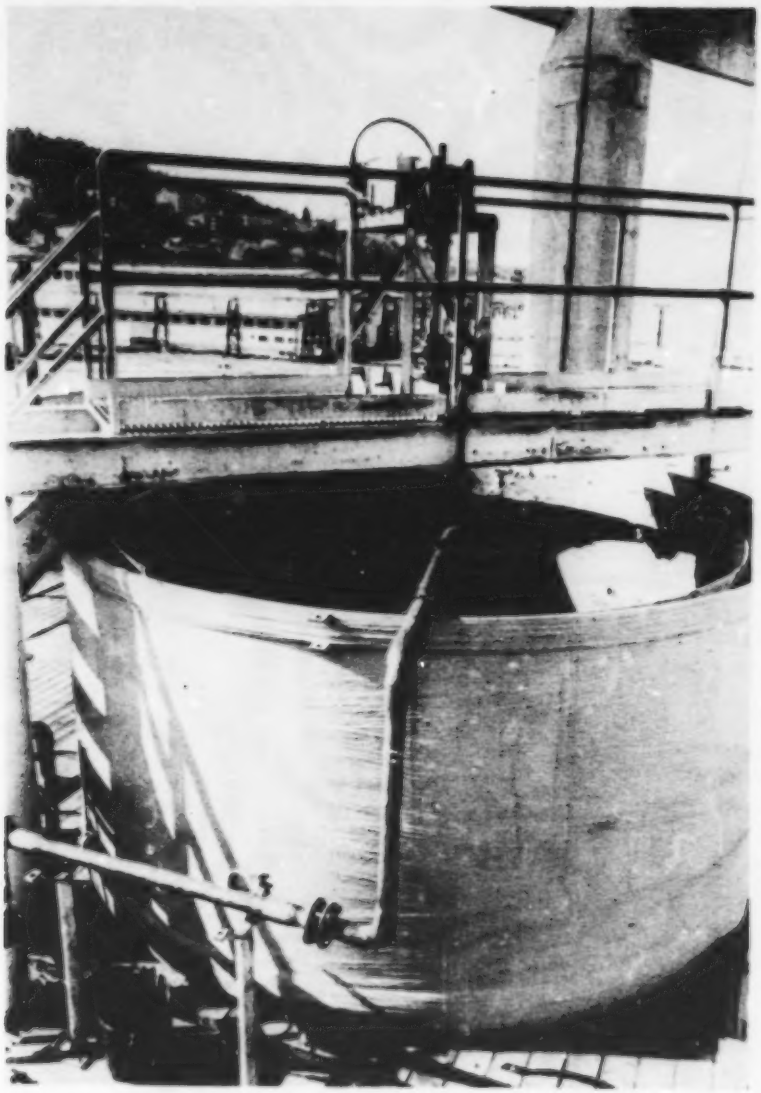


Figure 24. The 12' x 6' sludge thickener prior to the rotary vacuum filter in the sludge treatment system

Our plant instrument department designed and installed the remainder of the instrumentation for the sludge and sulfide system. The nearly completed plant is shown in Figure 25.

Start-up

The start-up team was selected during the construction phase and the start-up leader began operating and checking out the equipment as soon as each piece was completed. An operating manual was written for use in operator training (Appendix D).

As the start-up date approached, the start-up leader held several one-hour training classes with each operating shift, going over the process, the model, the desired operating procedures and the installation. Feedback from the operators was valuable in correcting minor problems apparent before start-up began.

Numerous problems were encountered during the start-up and were corrected, as discussed earlier. The start-up was divided into two parts since the water and sludge systems are nearly independent. The water treatment system was started up about two months prior to the sludge system.

INNOVATIONS AND NEW TECHNIQUES

Waste Water Treatment Innovations

In our laboratory work, and confirmed on a plant scale, the critical operations in the sulfide removal system are the control of pH and rapid filtration following the sulfide addition. The sulfide and filter aid addition equipment is shown in Figure 26.

Sludge Treatment Innovations

For our sludge, the furnace roasting process achieved Hg levels in the clinker 2 to 3 orders of magnitude lower than the lowest Hg levels possible after chemical treatment (Table 2 and Appendix A). Still further reductions could be achieved by acid treating the sludge before roasting, as shown in Table 7, although this method had the disadvantage of generating foam and lowered the fusion temperature of the clinker.

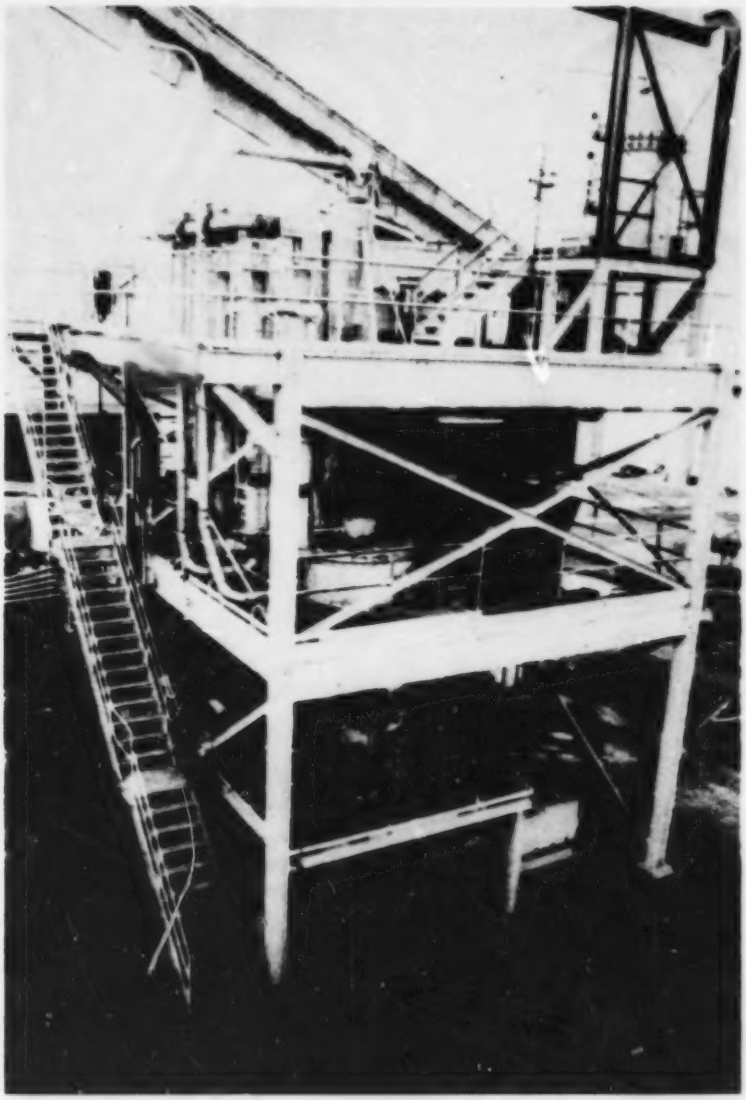


Figure 25. The full scale Hg Recovery System as installed at the Bellingham Chlor-Alkali Plant

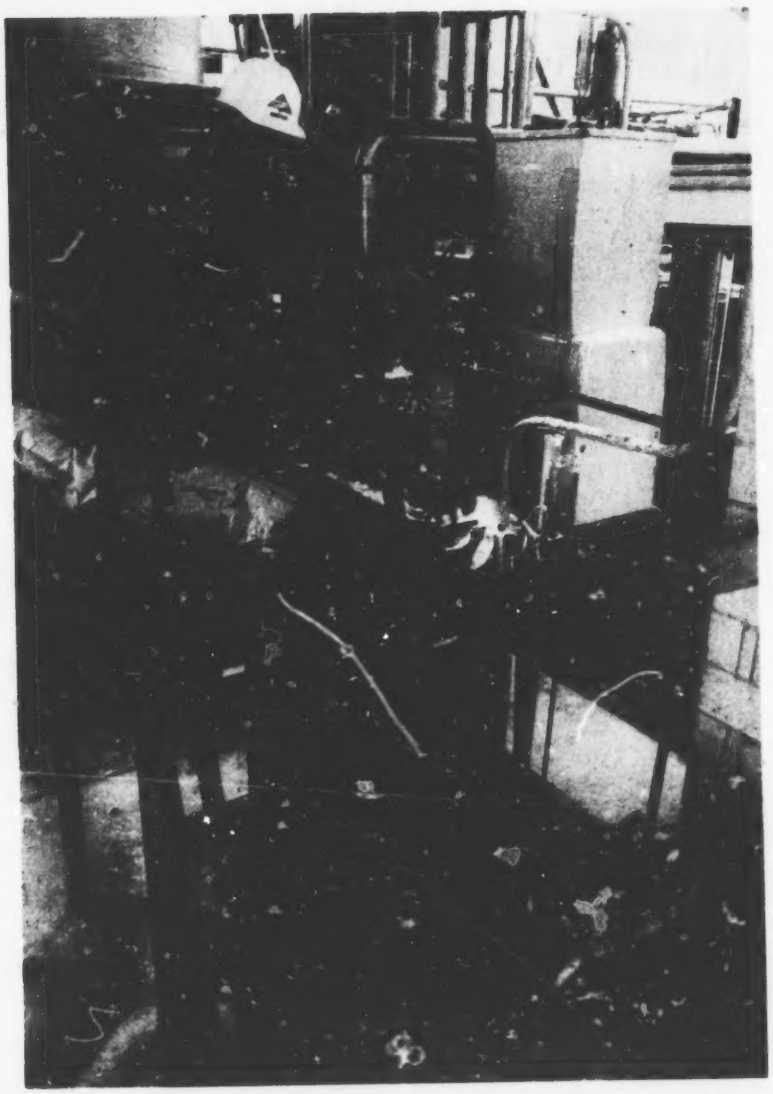


Figure 26. The mix tank in the sulfide precipitation system where the D. E. and sulfide are added

Prior to this work, it was reported that the brine sludge was too sticky to dewater with a rotary vacuum filter alone; a precoat filter would have been required, causing greater operating expense and requiring more operator attention. The pilot and full scale plants have demonstrated that our sludge dewaters easily on a rotary vacuum belt filter.

One further discovery was that the Hg present in the sludge was concentrated in the graphite particles present; the smaller particles had a much higher Hg content, 990 ppm, than the larger particles, 100 ppm,(Figure 27).

ECONOMIC ANALYSIS

Water Treatment System

The economics of the water treatment system are shown in Figure 20 and Table 20. The system as installed cost $143,900 to construct and will handle up to 570,000 l (150,000 gal) per day. The operating costs include chemicals, electricity, operator time and maintenance cost. These costs total $510 per week or 13¢/1000 l (50¢/1000 gal) at 380 l/min (100 gpm).

Sludge System

The cost of constructing the sludge system as shown in Figure 18 and Table 21 was $364,500. The system is capable of processing 7.3 m tons (8 s tons) of dry sludge per day at a cost of $280 per day or $32/m ton ($35/s ton) of dry feed. These operating costs include operator time, natural gas, electricity, and maintenance. The annual maintenance cost has been estimated at 15% of the capital cost. At this rate, the maintenance cost represents 60% of the total operating cost.

Figure 27. Particle distribution in brine sludge which was washed and screened to remove particles 0.007" diameter (Experiment 34)

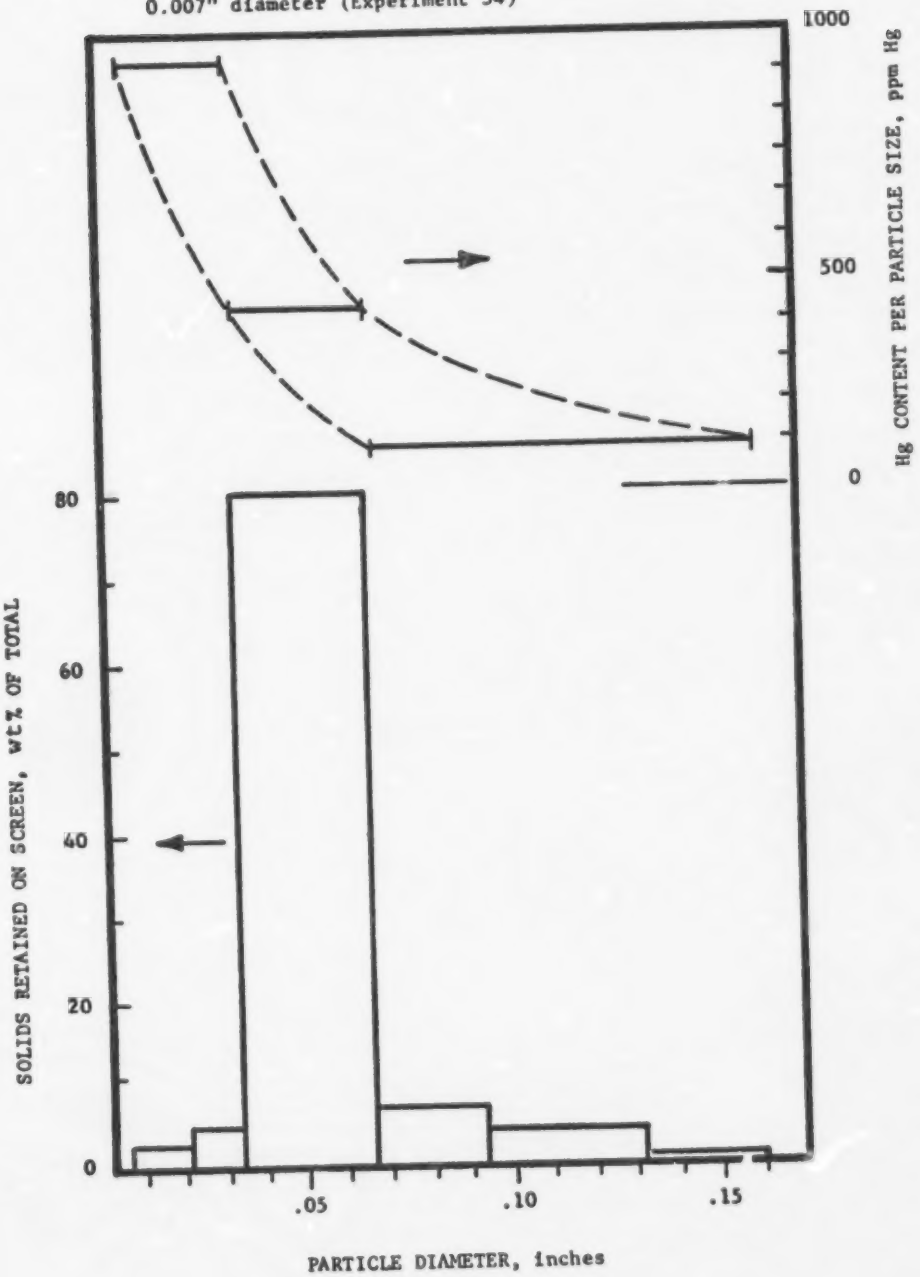


Table 20. COST ESTIMATE- WATER TREATMENT SYSTEM

Item Description	Labor	Materials	Total
Filter and installation	$ 3,000	$16,000	$19,000
Pumps	4,700	4,000	8,200
Instrumentation and controls	9,000	6,700	15,700
Tanks and vessels	3,100	5,600	8,700
Piping and valves	41,000	14,600	55,600
Electrical	7,000	4,000	11,000
Painting	1,100	460	1,560
Structure, ladders and platforms	8,700	4,400	13,100
		Subtotal	132,860
	Engineering at MH @ $10.00 MH		11,000
	Total investment required		$143,900

Table 21. COST ESTIMATE - SLUDGE SYSTEM

Item Description	Labor	Materials	Total
Multiple Hearth Furnace	$ 9,000	$58,000	$ 67,000
Rotary vacuum filter	2,700	26,000	28,700
Incinerated solids screw feeder	1,200	4,800	6,000
Sludge feed	4,000	7,500	11,500
Instrumentation and controls (System)	6,200	2,600	8,800
Furnace instrumentation and controls (Union Heating)			18,000
Sludge piping and thickener	28,000	19,000	53,000
Heat exchangers and associated off gas piping	6,300	22,000	28,300
Structure, ladders and platforms	31,000	14,000	45,000
Natural gas and water service	14,000	11,000	25,000
Site preparation and foundation	8,000	4,000	12,000
Pumps	3,000	8,000	11,000
Painting	8,000	2,200	10,200
Electrical	12,000	6,000	18,000
		Subtotal	342,500
	Engineering at MH @ $10.00 MH		22,000
	Total investment required		$364,500

SECTION VIII

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SECTION IX

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SECTION X

GLOSSARY

1. Body feed - A filter aid added continuously to the suspension to be filtered to keep the filter from plugging.

2. Brine sludge - Sludge resulting from chemical addition to sodium chloride brine to precipitate calcium and magnesium compounds and other impurities.

3. Cell anode - One of the electrodes in a Hg cell, made of graphite or metal.

4. Chlor-alkali plant - A plant producing chlorine and a metal hydroxide.

5. Diatomaceous earth - A meterial used to precoat filters and as a filter aid.

6. Effluent - The waste liquid discharged from a process.

7. Electrolytic oxidation - The generation of chlorine in a brine with electricity to cause oxidation of a desired material.

8. Hg - The chemical symbol for the element mercury.

9. Hg contaminated waste water - The waste water which comes in contact with Hg or Hg-containing material in a chlor-alkali process.

10. Mercury cell - The unit producing chlorine and a metal hydroxide from electricity and brine cathode.

11. Multiple hearth furnace - A direct fired furnace with trays on a vertical shaft.

12. Precoat - A filter aid added to coat the filter element before filtration begins.

13. Pressure filter - A filter which uses pressures greater than atmospheric pressure on the unfiltered side.

14. Polishing filter - A final filter which removes the last traces, following a preliminary filter.

15. Rotary calciner - An inclined cylinder heated and rotated; material is passed through the cylinder.

16. Rotary vacuum filter - A filter utilizing vacuum inside a cyclinder to pick up and dewater a cake on the outside of a drum.

17. Star valve - A rotating paddle wheel that allows solids to pass through but seals the opening against air leakage.

18. Thickener - A large continuously fed tank which concentrates or thickens a sludge to a higher total solids.

19. Untreated sludge - Chlor-alkali plant sludge as it comes from the process.

SECTION XI

APPENDICES

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APPENDIX A

HYPOCHLORITE, CHLORINE, AND ELECTROLYTIC OXIDATION

The object of the chemical oxidation trials was to convert Hg to the soluble mercuric ion in the presence of chloride ions to form the soluble mercuric tetrachloro complex. The overall reactions involved are as follows:

$$Hg + ClO^- + 3Cl^- + H_2O \rightleftharpoons HgCl_4^= + 2OH^-$$

$$2Hg^+ + ClO^- + 7Cl^- + H_2O \rightleftharpoons 2HgCl_4^= + 2OH^-$$

$$Hg^{++} + 4Cl^- \rightleftharpoons HgCl_4^=$$

Procedure

The trials were conducted using 250 ml to one l of brine sludge for each test. Trial conditions and results are shown in Table 22.

The hypochlorite oxidation trials involved mixing liquid sodium hypochlorite with a brine sludge in an agitated beaker for the time period specified. The treated sludge was filtered in a Buchner funnel and washed with 200 - 400 ml of distilled water before analyzing the washed sludge for residual Hg (Figure 28).

The chlorine oxidation trials were similar except that gaseous chlorine was sparged into the sludge from a cylinder of liquid chlorine.

Results

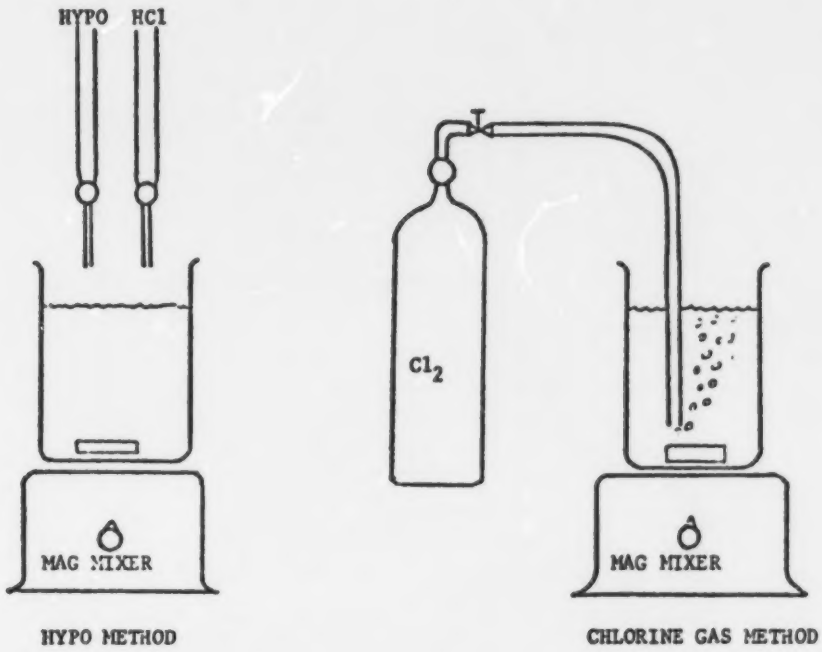
From the results of bench scale trials, the hypochlorite appeared to dissolve nearly as much sludge solids (60 - 80%) as Hg (60 - 86%). Thus, up to 90% of the Hg was removed, but the solid residue contains 100 - 300 ppm Hg. In the work of Tokawa (26), a one-stage hypochlorite extraction removed 40 - 70% Hg and 4 - 8 stages were needed to removed over 95% of the Hg (Table 23 and Figure 29).

Other investigators have suggested that the use of chlorine gas as the oxidizing agent would reduce residual Hg in the treated sludge to 1 ppm. In the 9 experi-

Table 22. OXIDATION OF BRINE SLUDGE USING SODIUM HYPOCHLORITE

Exp. No.	Hypo concentration, gpl Cl_2	pH	Reaction time, hr.	Temp., °C	Initial Hg content, ppm	Solids dissolved, %	Hg removal, %	Remaining Hg in solids, ppm, dry	Comments
1A	30	6.2	4	60	270			304	
1B	30	6.2	4	22	270			---	
1C	30	8.5	4	60	270			---	
1D	30	8.5	4	22	270			197	
2A	30	5.7-10	3	60	270			169	
2B	30	5.2-10	3	60	270			175	
3	30	7.3	4	60	270			110	2 stage
4A	90	11.2	3	60	270			≈100	
4B	90	11.2	3	25	270			≈100	
5	90	6.8-10.8	4	60	270			93	4 stage
6A	90	10.0	1	60	270		62%		
6B	90	9.0	1	60	270		64%		
6C	90	8.0	1	60	270		73.5%		
7	87	8.0	23	60	270			168	2 stage
8	89	8.0	1	60	270			≈258	Pressure reaction
12	190	8.0	1	60	150	76%	77%	140	
15	150	9.0	1	60	150	78%	86%	282	
17	150	8.0	1	60	4200	---	---	47	cell graphite
29	100	8.0	3	8-11	260	70%	76%	130	

Figure 28. Bench test set-ups for chemical oxidation of sludge



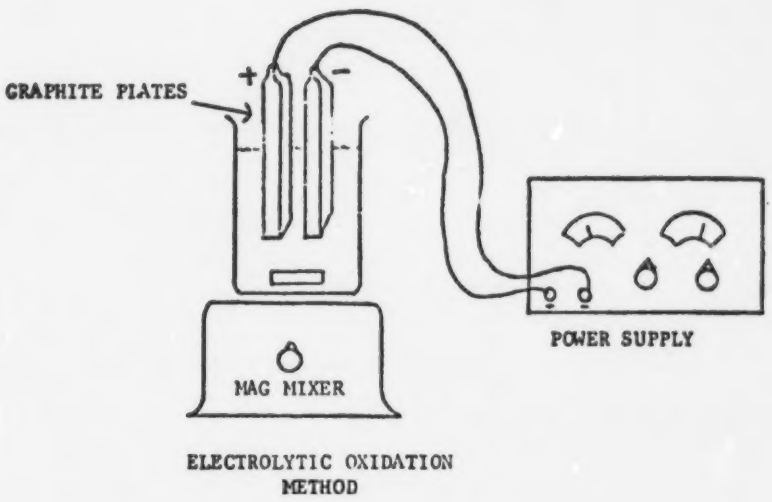
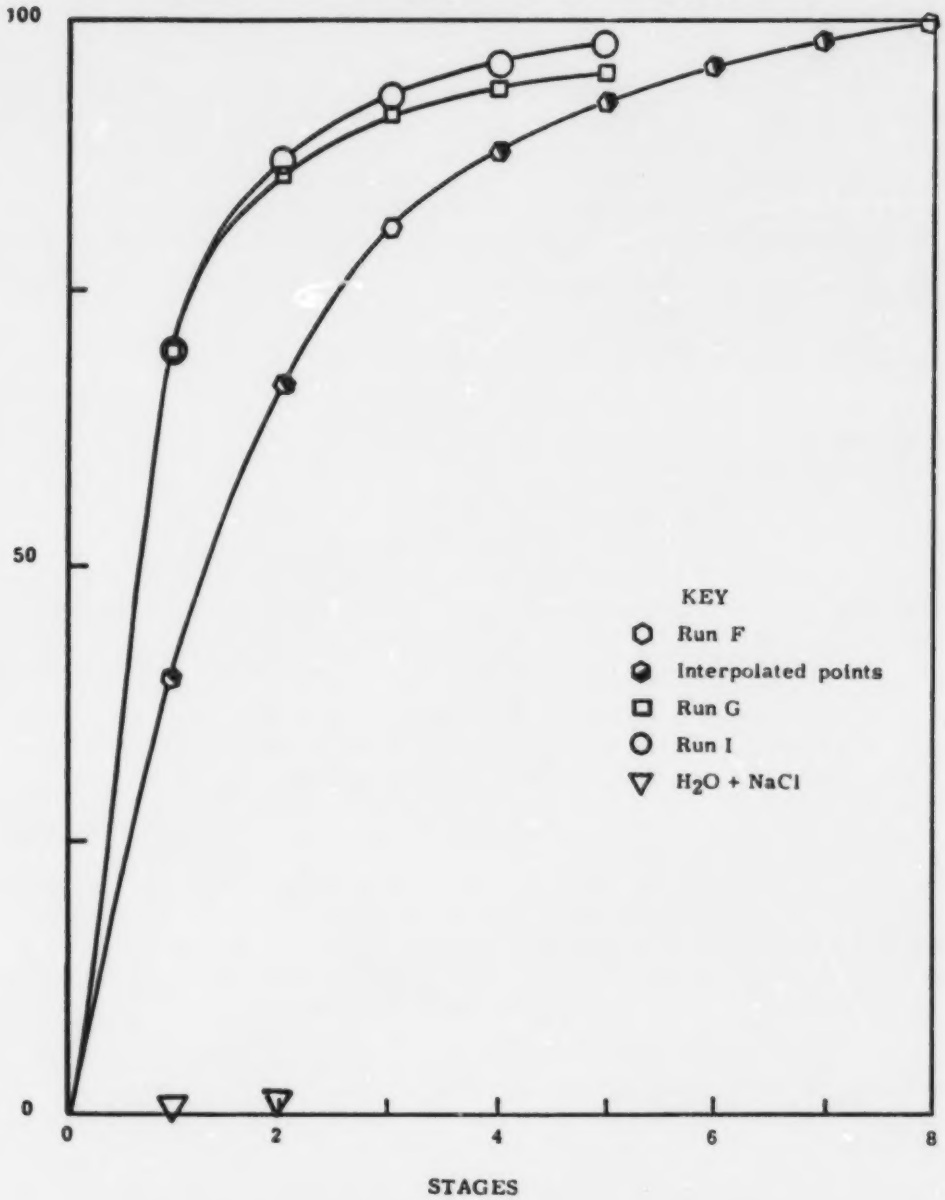


Table 23. OXIDATION OF BRINE SLUDGE USING SODIUM HYPOCHLORITE
WORK PERFORMED AT UNIVERSITY OF BRITISH COLUMBIA

Run No.	F		G		I	
Stage No.	Hg recovered, %	Hg remaining in sludges, ppm	Hg recovered, %	Hg remaining in sludges, ppm	Hg recovered, %	Hg remaining in sludges, ppm
START	--	3280	--	931	--	146
1	40%	1970	70	280	70	44
2	67	1080	86	130	88	18
3	81	620	91	84	93	10
4	87	430	94	56	96	6
5	92	260	95	47	97.5	4
6	96	130				
7	98	66				
8	99	33				

Figure 29. Effect of staging on mercury recovery by Tokawa



ments performed in these trials, half of the residues contained more Hg than the starting material (Table 24). The chlorination of the sludge dissolved 70 - 90% of the solids and approximately the same quantity of Hg so there was no net reduction of Hg concentration in the residual solids.

A sample of brine sludge from a chlor-alkali plant utilizing metal anodes was oxidized with hypochlorite and chlorine gas. Over 98% of the Hg was removed, leaving a solids residue containing 9.2 ppm Hg (Table 25). This suggests that metal anode sludges are susceptible to chemical conversion of Hg to the tetrachloro complex.

ALTERNATIVE Hg RECOVERY METHODS

A. Hypochlorite and Chlorine Oxidation

The initial work on extracting Hg from brine sludge was performed using sodium hypochlorite. This method was known to remove Hg as early as 1924 from Glaeser's work (27). Extensive work has been done on sodium hyopchlorite leaching of Hg from low grade ores by Parks (28, 29), Town (30) and others. Although Parks achieved a 96.4% recovery, there still as 10 ppm Hg left in the residue. Town was able to achieve a 99.8% removal by leaching of very concentrated ores (79%) but there remained 24,000 ppm Hg in the residues.

In Japan, this process has been used by 4 chlor-alkali plants for up to 5 years to remove Hg from brine sludge. This process has been marketed in the United States since 1970 by Crawford & Russell, who claim the process will remove 95% or more of the Hg from brine sludge (31). In a more recent publication, Crawford & Russell claimed a reduction of Hg in the dry sludge from 50 - 4000 ppm to 0.1 ppm via the hypochlorite leaching process with pH adjustment (32). From our work, the 95% Hg removal stated in their sales literature is more realistic than the 0.1 ppm Hg residual claimed.

The basis for this process is the conversion of elemental Hg and insoluble Hg compounds to water soluble mercuric ions with the OCl. The soluble stable complex $HgCl_4^{=}$ is formed.

Tokawa found that multistaging the extraction process could increase the Hg recovery to 99% with 8 stages (26). However, the maximum achieved in our laboratory in one stage was 86% recovery with a minimum final

Table 24. OXIDATION OF BRINE SLUDGE USING CHLORINE GAS

Exp. No.	Chemical	Time, hr	Start	End	Initial Hg content, ppm	% solids reduction	% removal	Remaining Hg in solids, ppm, dry	Comments
14A	Chlorine/Flotation	---	10.0	5.0	150	----	---	114	Foam Hg content
14B	Chlorine/Flotation	---	10.0	5.0	150	----	---	102	Solids
23	Chlorine	2.5	10.0	4.7	150	70.0	74	200	
24	Chlorine	5.0	5.0	4.1	150	86.5	83	163	Reducted pH to 5 before Cl_2
25	Chlorine	5.0	10.4	4.5	150	86.0	78	138	
26	Chlorine	1.75	10.3	4.0	150	----	45	314	
27	Chlorine	7.0	10.3	3.6	150	----		~400	
28	Chlorine	7.0	1.7	1.5	150	----		~400	Acid addition to pH 7
30	Chlorine	7.0	10.0	4.5	150	88.0	---	117	

Table 25. OXIDATION OF BRINE SLUDGE USING COMBINATIONS OF HYPO, CHLORINE, ELECTROLYTIC ACID TREATMENT AND ROASTING

Exp. No.	Conditions of test	Initial Hg content, ppm	% solids reduction	% recovery	Final Hg in solids, ppm, dry	Comments
9	H_2SO_4 + Hypo	137	---	88	65	
10	Electrolytic oxidation	150	---	--	111	
11	Hypo + electioxidation	150	---	--	120	
18	Hypo + chlorine gas	150	31	56	43	
29	HCl only	150	53	72	81	
20	Hypo + chlorine gas	4200	53	85	150	Cell graphite
21	Hypo after acid treatment	81	59	54	100	Acid treated
22	Hypo of roasted	0.26	50	17	0.2	Roasted
36	Leaching of roasted	1.7	---	--	3.0	Roasted
54	Hypo + chlorine	158	72.4	98.4	9.2	Metallic anode sludge (Wyandotte)

Hg content of 47 ppm. Due to the great difficulty and expense required to separate the liquid from the fine solids at each stage in a multistage extraction, a practical system would be restricted to a one- or two-stage operation. It became evident that the chemical equilibrium was not favorable to remove the residual 5 - 10% of the Hg in the sludge in one stage. The use of chlorine injections did not improve Hg conversion.

In the laboratory, graphite in the sludge was concentrated as the sludge was digested. In addition, the Hg concentration in the graphite particles was found to be 6 - 8 times higher than the Hg level in the remainder of the sludge (Table 26). From these and other data, we hypothesize that the graphite from the anodes and decomposer packing is a major contributor to the residual Hg after sludge digestion. This is further supported by the results from a sample of metal anode sludge (little graphite present) treated with hypo and chlorine (experiment 54 and Table 25). The final Hg level was 9.2 ppm compared to a sample of our sludge treated exactly the same (experiment 18, Table 25) which contained 43 ppm Hg after treatment.

The distribution of Hg content in our sludge of various graphite particle size groups is shown in Figure 27. Over 80 weight percent of particles are 0.76 mm - 1.8 mm (0.03 - 0.07 in.) in diameter. Moreover, the Hg content increases as the particle size decreases. This is consistent with an adsorption mechanism of Hg on the graphite, since the surface area increases with decreasing particle size.

Attempts were made to remove graphite from sludge, but abandoned for 3 reasons: (1) the sludge would still have to be treated for Hg removal; (2) removal of the very fine graphite particles with the highest Hg content was difficult and costly; and (3) to remove the graphite quantitatively from the sludge was not practical.

Table 26. Hg ANALYSIS OF BRINE SLUDGE SIZE FACTIONS

Sample Description	Hg content wet basis, ppm	Total solids, %	Hg content dry basis, ppm
Brine sludge before separation	45	35	270
Large graphite particles in sludge	646	40	1600
Remaining fines in sludge	26	10-15	175-250

B. Electrolytic Oxidation

A modification of the hypochlorite and chlorine oxidation methods for treating brine sludge is generation of hypochlorite ions during sludge treatment. This method has been used successfully by Scheiner (33) of the U. S. Bureau of Mines to extract 90 - 95% of the Hg from ores containing 300 - 10,000 ppm Hg. The electrolytic method simply uses dissolved sodium chloride in the sludge mixture to liberate chlorine gas when a DC voltage is applied across 2 graphite electrodes. Scheiner believes the tiny chloride gas bubbles formed and the reaction between Hg and chlorine at the surface of the electrodes provides a more effective oxidation than simple injecting chlorine gas or hypo into the slurry.

Our tests were performed in an apparatus consisting of 2 graphite plates with an area of 13 cm^2 (2 in^2) in a 1000 ml beaker spaced 2.5 cm (1 in) apart (Figure 20). A DC power source supplied current to the brine-sludge solution to generate chlorine gas from the sodium chloride present. The tests were not significantly more successful than the chemical oxidation methods; residual Hg levels in the remaining solids averaged 100 ppm.

APPENDIX B

DETERMINATION OF Hg

BY FLAMELESS AA

The procedure used to analyze samples for Hg during the course of this project was modified from an EPA method published in 1970. The complete procedure is described below.

I. Sampling

1. Rinse all glassware and polyethylene containers with dilute nitric acid and then with distilled water prior to use.

2. Acidify samples of water and effluent if they will stand more than one day prior to determination of Hg. Add 10 ml concentrated HNO_3 per 1000 ml sample.

II. Equipment

1. Rinse all glassware with dilute HNO_3 and then with distilled water prior to use.

2. Store glass beads in a small amount of concentrated HNO_3 and rinse with distilled water prior to use.

3. Modified A.O.A.C. digestion apparatus. Substitute single-neck 250 ml or 300 ml boiling flasks for the 3-neck digestion flask.

4. Perkin-Elmer Atomic Absorption Spectrophotometer, Model 303. AA settings: wave length, 254.5; range, UV; slit width, 3; source current, 10 ma; meter response, 1; scale, 1. Perkin-Elmer Recorder Readout: noise suppression, 2; scale expansion, x3. Airflow meter, set at 40. Align the gas absorption cell to allow maximum light to pass through. Allow equipment to warm up at least 20 minutes before using.

5. Aeration apparatus:

   a. Use Anhydrone (magnesium perchlorate) as the drying agent; change weekly or more often as needed.

CAUTION: If Anhydrone comes in contact with skin or clothing, wash area immediately with water. Magnesium perchlorate may cause severe burns to skin or may cause fire when in contact with clothing or combustible material.

b. Clean the gas washing bottle biweekly with a small amount of HF acid, rinse with water, and clean again with dichromate cleaning solution. Clean the sparger biweekly with boiling dilute HCl. Rinse apparatus thoroughly with distilled water prior to use.

CAUTION: Hydrofluoric acid liquid and vapor may cause severe burns which may not be immediately painful or visible. Do not leave glassware in contact with HF longer than is absolutely necessary.

c. Do not allow moisture to collect in the 17 cm gas absorption cell. If moisture does collect, dry cell thoroughly in a 105°C oven and change the drying agent in the drying tube.

III. Procedure

A. Preliminary treatment of sample: Use modified A.O.A.C. method for organic and solid samples and effluent: use modified F.W.Q.A. method for inorganic aqueous samples, caustic, and sulfuric acid.

1. Modified A.O.A.C. method:

Take suitable amounts of sample (not more than 100 ml or 5 g dry) to provide 0.1 - 1.5 µg Hg, place in a single-neck flask and treat each according to type of sample.

a. Samples

i. Mud, sludge, etc.
Add 10 ml distilled water to sample and then add 10 ml concentrated HNO_3 per g dry sample. Proceed with digestion as below (IIIA1b).

ii. Effluent
Proceed with digestion as below (IIIA1b).

b. Digestion procedure

To the single-neck flask containing the sample, add 20 - 25 ml 1:1 HNO_3 -H_2SO_4 and 3 - 4 glass beads. Attach flask to modified A.O.A.C. digestion apparatus. Carefully heat sample until it refluxes steadily; avoid losing gaseous NO_2 too rapidly. Collect condensate in extraction unit until digest reaches incipient boiling or goes to acid fumes.

If sample darkens or turns black, cool, and add more concentrated HNO_3.

Allow digest to cool; drain collected liquids back into flask, and reflux for 10 - 15 minutes to rid apparatus and sample of gaseous NO_2. (Add 25 ml distilled water to sample through condenser if NO_2 is difficult to remove. Reflux again for 10 - 15 minutes.) Cool sample and rinse condenser with two 10 ml portions of water.

It may be necessary here to dilute the sample to volume and take an aliquot of sample before proceeding.

Proceed with F.W.Q.A. sample treatment (IIIA2b).

2. Modified F.W.Q.A. method: Take suitable amounts of sample (not more than 100 ml) to provide 0.1 - 1.5 µg Hg, place in a 150 ml beaker containing 7 ml 1:2 HNO_3 -H_2SO_4 plus distilled water to make a final volume of 100 ml. Treat each according to type of sample.

a. H_2O, Cl_2 plant effluent, NaOCl, samples Proceed with modified F.W.Q.A. treatment as below (IIIA2b).

b. Modified F.W.Q.A. sample treatment

Dilute sample aliquot to 100 ml with distilled water. Add 1 ml 5% $KMnO_4$ and let sample stand for at least 15 minutes. Add 2 ml 5% $K_2S_2O_8$, allow sample to stand at

least 30 minutes and proceed with aeration step as below.

B. Aeration Procedure

Connect aeration apparatus to spectrophotometers; adjust spectrophotometer, flow meter, etc., as in II4. After allowing apparatus to warm up, adjust baseline and 100% absorption line with stopcock in bypass position. Proceed with aeration of sample, treating each sample individually as below. Carry out each step with as little delay as possible between steps:

1. Destroy excess permanganate with 2 ml 10% NH_2OH-HCl, and immediately wash the clear sample into gas washing bottle.

2. Add 5 ml 10% $SnCl_2$ to gas washing bottle. Immediately replace gas washing bottle in the aeration apparatus and turn stopcock to aeration position.

3. After pen has returned to within 2% absorption, turn stopcock to bypass; rinse gas washing bottle and proceed with next sample.

C. Calculations

A series of 6 standards ranging from 0.10 - 1.5 µg Hg is treated as for H_2O and Cl_2 plant sewer samples and is run each time the spectrophotometer is operated. Plot a calibration graph on semi-log paper with µg Hg on the linear scale and percent absorption on the log scale. Convert percent absorption of the sample to µg Hg and determine Hg content as follows:

$$\text{Hg, ppm} = \frac{(\mu\text{g Hg from graph})\ (\text{dilution in ml})}{(\text{g sample, note 1})}$$

IV. Notes

1. Assume specific gravity for volumetric samples to be 1.0 for dilute liquids, 1.5 for 50% caustic and 1.84 for sulfuric acid.

V. Reagents

1. Nitric acid-sulfuric acid, 1:1 mixture. Slowly

add 250 ml concentrated H_2SO_4 to 250 ml HNO_3 with constant stirring. Allow to cool before using; store in glass container. Caution: Wear safety glasses and gloves at all times during preparation of acid solution.

2. Nitric acid-sulfuric acid, 1:2 mixture. Follow procedure above using 150 ml concentrated HNO_3 and 300 ml concentrated H_2SO_4.

3. Potassium permanganate, 50 gpl. Weigh 50 g reagent grade $KMnO_4$ into a 150 ml tall-form beaker. Add approximately 70 ml distilled water and stir for about 20 seconds. Allow the $KMnO_4$ crystals to settle, and decant the supernatant liquid into a one liter volumetric flask. Repeat the operations of dissolving and decanting until all the $KMnO_4$ has dissolved. Dilute to volume, mix, and store in a brown bottle in a dark place.

4. Potassium persulfate, 50 gpl. Dissolve 20 g $K_2S_2O_8$ in 400 ml distilled water.

5. Hydroxylamine hydrochloride, 100 gpl. Dissolve 40 g NH_2OH-HCl in 400 ml distilled water.

6. Stannous chloride, 100 gpl. Dissolve 20 g $SnCl_2$-$2H_2O$ in 20 ml concentrated HCl on the hot plate. Cool and add 180 ml distilled water. Prepare weekly or more often as needed. If solution becomes discolored, cloudy, or turns the sample solution cloudy upon addition (prior to aeration), discard and prepare a fresh solution.

7. Stock Hg solution, 1000 ppm. Dissolve 0.6768 g mercuric chloride ($HgCl_2$) in a 500 ml volumetric flask. Add 5 ml concentrated HNO_3 and dilute to mark with distilled water.

8. Working Hg standard, 10 ppm. Dilute 5.0 ml 1000 ppm Hg to 500 ml with distilled water plus 5 ml HNO_3. Prepare bimonthly.

9. Working Hg standard, 0.5 ppm. Dilute 25.0 ml 10 ppm Hg to 500 ml with distilled water plus 10 ml HNO_3. Prepare monthly.

VI. References

1. William Horwitz, Ed. "Official Methods of Anal-

ysis of the Association of Official Agriculture Chemists," 9th edition, Association of Official Agriculture Chemists, Washington, D.C., 1960, pp. 327-330.

2. Federal Water Quality Administration, Provisional F.W.Q.A. Method for Hg Determination by Flameless AA, 1970.

3. Dow Chemical Company, Determination of Mercury by Atomic Absorption Spectrophotometric Method, 1970.

APPENDIX C

ALTERNATE Hg RECOVERY METHODS

Reduction Methods

A method much discussed in the literature, and in commercial operation, is the reduction of the mercuric ion to the metallic state followed by physical removal of the Hg particle by filtration (2, 25, 34, 42). Diverse materials may be used to perform this reduction but all rely using a suitable reducing agent. Some of the chemicals proposed or used are:

1. Hydrazine hydrate
2. Aldehydes
3. Sodium borohydride
4. Sodium amalgam
5. Metals: zinc, iron, bismuth, tin, nickel, magnesium, manganese, copper, aluminum, tin chloride.

The Ventron process utilizes sodium borohydride as the reducing agent. This process was installed at the Sobin Chlor-Alkali Plant in Orrington, Maine, and at the Ventron Plant in Wood-Ridge, New Jersey. A. 99.5% Hg removal efficienty was reported. In lab tests, we were not able to achieve Hg removals as great (Table 19). The differences may be explained by varying conditions between our tests and Ventron's or by the difference between our waste water and the Sobin waste water.

In any case, the equipment required is similar to that needed for sulfide precipitation: a pH adjustment system, a reducing chemical addition, and a filtration step with or without filter aid (Figure 10).

The main advantage of the Ventron process is that Hg can be recovered in the metallic state and reused without further processing. However, to achieve the 99.5% recovery as claimed, the reduction step must be followed by a carbon bed and a resin bed for polishing. In our laboratory tests, the reduction step using sodium borohydride alone produced recoveries in the 95 - 98% range (Figure 19). With these efficiencies, the reduction

and filtration process could be used alone in plants producing 100 - 200 tons per day of chlorine but large plants would have to add the polishing step (Table 27).

The cost of the sodium borohydride is about $16.50/kg ($7.50/lb). Excess addition of chemicals or concentrations of other ions which consume $NaBH_4$ could create high operating costs. Theoretically, one kg of $NaBH_4$ could reduce up to 21 kg of Hg if no intefering substances are present. However, any oxidizing chemicals such as available chlorine or metal ions capable of being reduced would consume $NaBH_4$.

Other reduction methods tried successfully have involved a number of chemicals. One of the most common is zinc. In work performed at Merck, Sharp and Dohme by Rickard and Brookman (40), a 99% Hg removal was reported using a dosage level of 3.8 kg zinc per kg of Hg. In our laboratory work, we have achieved recoveries of 95 - 99.8% using zinc particles in a column, followed by filtration. To separate the Hg from the zinc, a distillation step is required, in common with most other methods of Hg precipitation or adsorption. An additional problem associated with this method is residual dissolved zinc in the effluent, ranging from a few to a few hundred ppm zinc depending on the pH of the effluent. The background level of zinc in seawater is 0.01 ppm, and as with other heavy metals, biological concentration has been reported up to 1500 ppm. Therefore, if the zinc process is to be used, some method of zinc ion removal would be required. Such a process would add to the cost and complexity of the system; therefore, no further studies are contemplated on zinc treatment systems.

Many other metals have been tried with results similar to those reported for zinc, but the toxicity problem of dissolved metal ions is present to varying extents for each alternative. Of the least toxic metals tried, such as magnesium and iron, the cost of the metal is high or its effectiveness low (Table 28).

Laboratory studies are reported with other reducing chemicals such as hydrazine hydrate, aldehydes and others. Although we have not studed these, we believe the same problems and advantages hold as for sodium borohydride.

Table 27. Hg REMOVAL RATES NECESSARY FOR VARIOUS SIZE CHLORINE PLANTS TO ACHIEVE 45 gm (0.1 lb) PER DAY MERCURY IN THE EFFLUENT

Plant size Cl_2/day		Estimated[1] Hg contaminated water volume,		Calculated[2] final Hg level,	Reduction[3] through treatment,
m ton	s ton	l/day	gpd	ppb	%
90	100	75,000	20,000	600	94.0
180	200	150,000	40,000	300	97.0
360	400	300,000	80,000	150	98.5
740	800	600,000	160,000	75	99.3
1450	1600	1,200,000	320,000	38	99.6

[1]Volume estimated on the basis of 75,000 l/day (20,000 gpd) of contaminated waste water per 90 m ton (100 s ton) chlorine production per day.

[2]Maximum effluent concentration to achieve level of 45 gm/day (0.1 lb/day) Hg in effluent.

[3]Assuming the starting Hg level in waste water was 10 ppm Hg.

Table 28. COMPARISON OF SUBSTANCES USED OR CONSIDERED FOR REDUCING MERCURY ION IN SOLUTION

Compound or metal	Effectiveness[1]	Cost[2] $/kg	Cost[2] $/lb.	Toxicity[3] potential
Sodium borohydride	High	16.50	7.50	--
Bismuth	?	19.80	9.00	--
Tin	Low	9.35	4.25	Medium
Nickel	Low	3.56	1.62	High
Hydrazine hydrate, 85%	High	1.50	.68	---
Magnesium	High	.84	.38	Low
Copper	Low	1.50	.68	High
Maganese	High	.84	.38	Low
Aluminum	High	.68	.31	Medium
Zinc	High	.77	.35	High
Iron	Low	.22	.10	Low
Sodium sulfide[4]	High	.15	.07	High

[1] Based on Standard Oxidation Reduction Potentials.

[2] From "Chemical Marketing Reporter", April 8, 1974; "Metals Week", April 29, 1974.

[3] Subjective information from Water Quality Criteria, F. W. P. C. A., U. S. Department of the Interior, April 1968.

[4] Not a reducing agent.

The use of sodium amalgam to reduce Hg in brine or waste water has been tried by Karpink with limited success (35, 36). The 78% reduction reported is too low for this system.

Ion Exchange & Chelating Resins

Another method for removing Hg from waste water that appears frequently in the literature and has been used in several plants in Japan is the use of ion exchange or chelating resins (43 - 61).

The literature states that starting with Hg levels in the 2 - 30 ppm range, after one stage of resin treatment, the effluent contains 0.1 - 0.5 ppm Hg. With the addition of a polishing resin step, the effluent can reach 0.001 to 0.020 ppm (Table 16). Similar results have been achieved in our laboratory tests. With a starting solution of 10 ppm, the effluents range in concentration from 0.3 - 1.8 ppm. But when the starting solution is low in Hg, less than 0.1 ppm, which simulates a polishing step, the final Hg levels are 1 - 4 ppb (Figure 19 and Table 17). Resins tested in our laboratory work were from the Billingsfors-Långed and Ajinomoto companies and were specifically designed for Hg removal. Of the two resins tested, the Ajinomoto resin gave more consistent results.

Activated Carbon

Another means of removing Hg from waste water streams is to pass the water through a bed of activated carbon to adsorb the Hg onto the carbon particles. This principle has been used extensively for the removal of Hg from caustic soda using a finely divided carbon, such as Nuchar KD Special, as a precoat on a pressure filter. In this application, the Hg concentration is lowered from 2000 ppb down to 100 ppb.

Although the literature contains fewer references to work with activated carbon than resin, the experience in our laboratory indicates that activated carbon achieves nearly the same Hg removal rates as ion exchange resins (Figure 19). Effluent levels of 100 - 300 ppb Hg were achieved with starting Hg levels >10 ppm. However, with starting Hg levels below 0.1 ppm, the effluent contained 5 - 7 ppb. Of the 3 carbons tried, the Westvaco Nuchar 722 gave the lowest Hg levels in the effluent (Table 18). The bed capacities of the carbons were not determined.

As with the ion exchange resin, there are several problems which must be considered with such a system. They include: (1) periodic regeneration or replacement of carbon, (2) Hg recovery process from regenerant or spent carbon, (3) prefiltration of the treated stream to minimize bed plugging, and (4) determination of bed capacity and Hg leakage point.

Thus, the use of activated carbon for Hg removal seems more appropriate as a secondary polishing step rather than a primary process.

APPENDIX D

START-UP MANUAL

SLUDGE TREATMENT SYSTEM

Start-up

Note: Start-up requires a controlled sequence to have each piece of equipment ready when needed. It takes 8 hours after the starting the sludge pump to the thickener before the rotary vacuum filter and furnace will have to handle product. The furnace takes 48 hours to preheat to operating temperatures, so plan your time accordingly.

I. Sludge Dewatering (Assume brine clarifier is in operation.)

A. Brine Sludge Thickener

1. Close drain valve on thickener.

2. After determining there are no potential obstructions, start the rake on the thickener.

3. Open manual valves before and after sludge pumps.

4. Start pump by adjusting air valve on pump. Adjust valve on oil reservoir.

B. Gas Cooler Condensers

1. Open all manual valves so the gas can pass through bodies 1, 2, and 3 from top to bottom.

2. Start cooling water to each body.

3. Start induced draft fan.

C. BSP Envirotech Furnace

Upstairs Control Room

1. Turn on master control switch at the remote station.

2. Turn all burner control switchs to "on" positions at the remote station.

3. Manually adjust controller valves to "0" supply.

Downstairs at Furnace

4. Start shaft rotation.

5. Start shaft cooling fan.

6. Start combustion air fan.

7. Push reset switch (indicating shaft rotation has been reset).

8. Turn master gas control switch to "automatic". Purge timer light should come on; timer is set for 5 minutes.

9. Reset low and high pressure gas meters. When purge complete light comes on, proceed to next step.

10. Open manual gas valve.

11. Start the burner on low fire on No. 6 hearth.

12. Adjust temperature controller to 400 - 500°F. When stabilized, adjust controller upwards slowly (about 100F° per hour) until No. 6 hearth has a temperature of 1000°F.

13. Start burners on No. 5 hearth.

14. Adjust temperature controller to 400 - 500°F. When stabilized, adjust controller upwards slowly (about 100F° per hour) until No. 5 hearth has a temperature of 1000°F.

15. Start main burners on No. 4 hearth.

16. Adjust temperature controller to 400 - 500°F. When stabilized, adjust controller upwards slowly (about 100F° per hour) until No. 4 hearth has a temperature of 1000°F.

17. Start burners on No. 3 hearth.

18. Adjust temperature controller to 400 - 500°F. When stabilized, adjust controller upward slowly (about 100F° per hour) until No. 3 hearth has a temperature of 1000°F.

19. Start increasing temperature on all four hearths at the rate of 50F° per hour. Operating temperature is between 1400 - 1500°F.

Upon reaching operating temperature of 1400 - 1500°F, prepare rotary vacuum filter for operation.

D. Eimco Rotary Vacuum Filter

1. Close the filter vat drain valve.

2. Open the wash water line to the cloth and rolls.

3. Begin taking up the slack in the filter belt, being sure to adjust the ends of the takeup rolls equally.

4. Start the filter drum drive and completely soak the cloth, while retensioning the belt. When the takeup roll is at normal operating position, stop the filter drive.

5. Start the vat agitator. This should be operated at all times when the sludge is in the vat.

6. Turn on the seal water to the vacuum pump and filtrate pump.

7. Start discharge conveyor from furnace.

8. Start furnace feed conveyor.

9. Turn on feed to filter.

10. When sludge level in the vat reaches 30% full, start the vacuum pump, filtrate pump, and filter drive.

11. Adjust the filter drum speed and rate of feed as may be necessary for cake thickness, cake dryness, and removal from cloth.

It may take 40 - 60 minutes before sludge begins coming out the discharge conveyor. Check clinker for dryness and plugging of furnace.

SHUTDOWN

I. Sludge Dewatering

A. Brine Sludge Thickener

1. Shut manual valve from bottom of clarifier before pump. Flush fresh water through pump inlet and outlet to thickener.

2. After clear water appears at thickener. shut off sludge pump and drain water from line.

3. Continue to dewater sludge until consistency is too low for good filter performance. Divert the rest of the sludge to pond by shutting off filter feed and opening line to pond.

B. Eimco Rotary Vacuum Filter

1. Fully open all wash water to the filter belt.

2. Open vat drain valve. Flow will divert to pond.

3. Stop filtrate pump and vacuum pump, and shut off seal water.

4. Rotate drum drive at least 5 revolutions until filter cloth is clean. Then stop filter drive and shut off wash water. Note: Never leave a cloth to dry unless it is washed thoroughly.

5. Release the tension on the filter cloth by

turning the takeup roll cranks equally. Note the number of turns of the adjusting cranks so that the takeup roll can be returned to its original position at start-up.

6. Flush the wash trough with a small amount of fresh water. If shutdown will be longer than 8 hours, flush the filtrate tank and wash down the filter.

   Note: It will take 2 hours after the belt conveyor has delivered the last little bit of solids into the furnace, before the last clinker is discharged by the clinker conveyor. When the clinker conveyor is empty, begin shutting down the furnace.

C. BSP Envirotech Furnace

1. Start reducing the temperatures on all four hearths at the rate of 50°F per hour. When temperatures have stabilized at 900 - 1000°F continue to next step.

2. Adjust the temperature controller on No. 3 hearth so the temperature drops at the rate of 100°F per hour. When temperature stabilizes at 400 - 500°F turn off burner on No. 3 hearth.

3. Adjust the temperature controller on No. 4 hearth so the temperature drops at the rate of 100°F per hour. When temperature stabilizes at 400 - 500°F turn off burner on No. 4 hearth.

4. Adjust the temperature controller on No. 5 hearth so the temperature drops at the rate of 100°F per hour. When temperature stabilizes at 400 - 500°F turn off burner on No.5 hearth.

5. Adjust the temperature controller on No. 6 hearth so the temperature drops at the rate of 100°F per hour. When temperature stabilizes at 400 - 500°F turn off burner on No. 6 hearth.

Furnace temperature should be between 300 - 400°F. A decision at that time will be made whether to shut off the pilot or not. It is advantageous to keep the furnace at this temperature if possible.

D. Gas Cooler Condenser

As long as furnace is running on pilots or burners, the cooler condensers will remain in operation.

WATER TREATMENT

Start-up

I. Water Treatment

A. Acid Mix Tank

1. Open valve on the inlet to Hg waste water storage tank.

2. Open recycle valves to pH mix tank.

3. Open valve from spent acid stream.

4. Adjust level controller.

5. Open valves on inlet and outlet of the pond pump to mix tank.

6. Start flow from pond.

7. Adjust pH controller and start acid flow. Liquid in tank will continue to recycle until appropriate level is reached.

8. Start the agitator in the Hg waste water storage tank when the level is above the agitator.

B. Na_2S Storage Tank

1. Open valves on the outlet of the Na_2S storage tank.

2. Adjust rotometer to required gph.

C. R. P. Adams Pressure Filter

1. Open accept valve to sewer.

2. Open valve for filter feed.

3. Make sure bottom valve to backwash tank is closed.

D. Filter Aid and Precoat Mix Tank

1. Open valves on outlet and inlet of feed pump to filter.

2. Adjust level controller in mix tank.

3. Adjust BIF feeder to the rate of 1 oz/100 gal.

4. Adjust flow indicator from Hg waste water storage to mix tank. Remember, the flow should agree with the setting on the Na_2S addition system.

5. Start flow from Hg waste water storage tank.

6. Adjust Na_2S flow on rotometer.

7. Start BIF feeder. Initial start-up requires 50 lb. of diatomaceous earth.

8. Start agitator.

Note: When level has reached the controller set point, it will begin feeding filter at the rate you set at the flow indicator from the Hg waste water storage tank.

WATER TREATMENT

Shutdown

I. Water Treatment

A. Acid Mix Tank

1. Shut off pond pump to mix tank.

2. Shut off other flows to mix tank.

3. Shut off acid flow.

Note: If shutdown is only temporary, you can pump for a short time to the waste water storage tank. Be sure to treat with acid first.

B. Waste Water Storage Tank

1. When level is below agitator, shut off agitator.

2. Close valve out of tank.

Note: If waste water is to be stored in tank, leave on agitator.

C. Filter Aid and Precoat Mix Tank

1. Turn off BIF feeder.

2. Turn off rotometer from Na_2S storage tank.

3. Adjust level controller such that you can pump the remainder of tank through the filter. Then turn off pump.

4. Add fresh water and flush lines and pumps.

D. R. P. Adams Pressure Filter

1. Main objective now is to backwash filter:

   a. Close the feed valve from precoat mix tank.

   b. Open dump valve to backwash tank. Filter will drain to decant tank and majority of precoat should fall off by reverse flow.

   c. Refill tank 3/4 full with fresh water. Turn off water flow.

2. Pressurize filter with about 50 psi, then turn off air.

3. Open backwash valve quickly. The compressed air head should push the liquid in the reverse direction, thoroughly purging the filter tubes of any remaining cake.

Note: The receiver dump will be full of water and filter aid. Decant off water and open dump receiver to filter. Time required will be determined after initial start-up.

OPERATING NOTES

I. Sludge Dewatering

A. Thickener

1. A low level alarm on the thickener may indicate an insufficient pumping rate. If problem cannot be quickly corrected, notify the Tour Foreman. Note time period of trouble in log book.

2. There is a screen on top of the thickener to prevent larger size particles from entering the thickener. This should be cleared once a shift.

B. Rotary Vacuum Filter

1. In general, vacuum will be kept at a maximum and not varied in order to achieve maximum dryness.

2. Vat level and drum speed determine cake thickness and production rate. Level will generally be kept constant and speed varied. High speeds will tend to decrease dryness.

3. If filter will not pick up cake:

a. vat consistency may be too high

b. vat level may be too low

c. vacuum may be too low

d. the cloth may not be getting cleaned properly

4. In order to obtain dryer cake:

a. slow down the filter

b. decrease cake thickness (lower at vat level)

c. increase vacuum

5. The vacuum pump can be severely damaged if it is operated without seal water. Thus, the seal water should be adjusted or checked every 4 - 6 hours.

6. If the filtrate is not removed from the receiver, it will carry over to the vacuum pump. Check to see that the valve on the filtrate pump is wide open at all times.

7. Check cloth appearance frequently. Improper slack in cloth or misalignment can cause lack of vacuum or tearing of cloth. It is very important to correct these problems immediately.

C. BSP Envirotech Furnace

1. Monitor temperatures on all four hearths. It is important that we maintain an operating range of 1400 - 1500°F. Problems of insufficient temperature could be:

   a. combustion air fan

   b. improper gas to air ratio

2. Check shaft cooling fan regularly. This is vital for good operation of furnace.

3. It is important that we maintain an even flow to and from the furnace. If feed rate is too fast, plugging of upper hearth can and will be a problem. If this does happen, discontinue feed to furnace until incinerated solids conveyor is empty - possibly 4 hours - then continue operation.

D. Cooler Condensers

1. It is important that we receive the maximum amount of cooling from each condenser. If scale begins building up within the condensers, poor heat transfer will result in higher air temperature at the induced draft fan. These temperatures will be monitored each shift until a temperature range for operation is established.

2. Check induced draft fan frequently. Note excessive vibrations or other problems which might develop.

II. Liquid Treatment

A. pH Adjustment

1. If pH becomes a problem, check the following:

a. acid feed pump

b. acid fitters

c. automatic control valve

d. make sure agitator is operating

Note: pH should be maintained between 5 - 8. As you approach the higher pH's, Hg becomes more soluble and tends to pass through the filter media more easily. Also, lack of pH control tends to disrupt sewer pH.

B. Sulfide Precipitation

1. Excess sulfide is needed to precipitate Hg in the mix tank. Therefore, it is important that we maintain a proper flow and the right concentration of Na_2S to the mix tank. Check these often.

C. R. P. Adams Filter

1. It is important that the tubes within the filter are properly precoated. Improper precoating can cause tubes to plug and eventually break when backwashing.